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Asymptotic estimates on uncertainty of the elastic moduli of completely random trigonal polycrystals

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Abstract

Because of the uncertain irregular microgeometry, a random polycrystalline aggregate (the shape and crystalline orientations of the constituent anisotropic grains of which are uncorrelated) may have elastic moduli scattered over some, though small, intervals, while the conventional macroscopic homogeneity and isotropy hypotheses for it may be considered only as approximate with corresponding uncertainty. Our formal bounds are proposed to provide the estimates on those uncertainties in asymptotic sense. Explicit expressions for the aggregates of trigonal crystals (classes $3m$, 32, $\bar{3}m$) are derived.

Keywords: Elastic moduli; Completely random polycrystal; Trigonal crystal

1. Introduction

Many technical homogeneous and isotropic materials with tabulated macroscopic elastic moduli (measured directly from experiments) on microscopic scale are random polycrystalline aggregates. Macroscopic (effective) properties of those aggregates depend upon the properties of the base crystal as well as the polycrystalline microgeometry. In polycrystal forming processes, the constituent crystals are often formed independently at random places and grow till they meet each other. The kinematic constraints, boundary traction, friction, and inertia would not allow the crystals to turn over and fit together to make a configuration with minimal surface energy (as to form a single big crystal), but leave the primary crystalline orientations of the grains intact and accommodate them with the help of various defects on their common boundary (such as dislocation walls...). Hence it appears that the shape and crystalline orientations of the constituent grains in a random aggregate are uncorrelated. There may be competing tendency to some local correlation due to surface energy and anisotropic structure of the crystals; however, overall disorder and randomness seems to prevail and the randomness hypotheses can be considered as good approximation in many cases. This randomness makes the aggregate's effective moduli isotropic and so definite that they can

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be tabulated for applications, while all possible artificial well-ordered combinations of crystals may have a wide range of macroscopic properties including the same anisotropic ones as those of the base crystal (Avellaneda et al., 1988; Milton and Kohn, 1988; Avellaneda and Milton, 1989). Simple arithmetic (Voigt, 1928) and harmonic (Reuss, 1929) averages, or more sophisticated self-consistent approximations (Bruggeman, 1935; Landauer, 1952; Sermergor, 1977; Kröner, 1980; Norris, 1985; Pham, 1998; Pham and Phan-Thien, 1998) are often used to relate the grains' and aggregate's properties. However no available formula can give the precise value of a macroscopic property of a random polycrystal, except for very few cases where a property is independent of aggregate's geometry. The irregular and random nature of polycrystalline microgeometry makes the mathematical problem of finding the exact values of the effective moduli intractable. In addition, contrary to the conventional viewpoint, the effective properties of a random polycrystal may be not unique to be determined even in principle. There is no mathematical proof of uniqueness of elastic moduli of a random polycrystal, though one often takes it as a hypothesis. Available experimental data seem only to suggest that the polycrystalline material moduli are close to be unique such that they can be tabulated for technical uses (as certain numbers with just a few significant digits). Hence, in addition to the approximation schemes, the more refined approach to the problem is to construct upper and lower bounds on the possible values of the effective properties (Hill, 1952; Hashin and Shtrikman, 1962; Beran, 1968; Miller, 1969; Silnutzer, 1972; Zeller and Dederichs, 1973; Elsayed, 1974; Sermergor, 1977; Williemse and Caspers, 1979; McCoy, 1981; Phan-Thien and Milton, 1983; Pham, 1993, 1994, 1996, 1997, 2000a,b, 2001; Pham and Phan-Thien, 1998). A strategy to derive the bounds is to substitute appropriately constructed trial strain and stress fields into the minimum energy and complementary energy principles, exploring statistical hypotheses for a random aggregate. Our formal bounds (Pham, 2000b) appear the tightest available ones for the elastic moduli of a completely random polycrystal. They will be presented in the condensed form in the next section. In Section 3 we derive particular expressions of the bounds for the aggregates of trigonal crystals (classes $3m$, 32, $\bar{3}m$). A compromise in interpreting the bounds as the measure of uncertainty in observed elastic moduli of a random polycrystal will be presented in the last section.

2. Upper and lower bounds

In Pham (1993, 1997, 2000b) we consider a random polycrystal as a multicomponent material, each component of which is composed of the crystals of the same crystalline orientation (the number of the equal-volume components increase afterward to infinity to cover all possible orientations). The bounds are deduced from the minimum energy and complementary energy principles by substituting in them polarization trial fields (9)–(11) and (20)–(21) of Pham (2000b)—similar to those fields of Hashin and Shtrikman (1962); however, we do not use Hashin–Shtrikman specific variational principles. To evaluate the bounds, we presume the statistical isotropy and symmetry hypotheses (5) and (19) of Pham (1997): Statistical isotropy hypothesis (needed also for derivation of Hashin–Shtrikman bounds) requires that certain tensor integrals formed from spacial differentiation of harmonic potentials of unit density taken upon components' geometry of the aggregate be isotropic. Statistical symmetry hypothesis requires that an interchange of the spaces between any two components of different crystalline orientations should not alter overall characteristics of the random polycrystal. Alternative hypotheses on symmetric cell polycrystals having a similar sense have been taken in Williemse and Caspers (1979), Pham (2000a).

Let $\mathbf{C}$ denote the fourth-rank elasticity tensor of the base crystal of a polycrystal with components C_{ijkl}; $\mathbf{C}^{e}$—the effective elasticity tensor defined on an aggregate representative element (in large limit compared to the sizes of the constituent grains such that no size effect could be presented). The formal bounds on $\mathbf{C}^{e}$ can be given in the form (Pham, 2000b)

$$\boldsymbol{\varepsilon} : \mathbf{P}(\mathbf{C}, \mathbf{C}^{*}) : \boldsymbol{\varepsilon} \geqslant \boldsymbol{\varepsilon} : \mathbf{C}^{e} : \boldsymbol{\varepsilon} \geqslant \boldsymbol{\varepsilon} : \mathbf{P}(\mathbf{C}, \bar{\mathbf{C}}^{*}) : \boldsymbol{\varepsilon} \tag{1}$$

for all symmetric second-rank strain tensor $\boldsymbol{\varepsilon}$, where

$$\begin{aligned}
&\mathbf{P}(\mathbf{C},\mathbf{C}^*) = \mathbf{T}(P_k, P_\mu),\\
&P_k(\mathbf{C},\mathbf{C}^*) = [(\mathbf{C}+\mathbf{C}^*)^{-1}_{iijj}]^{-1} - k_*,\\
&P_\mu(\mathbf{C},\mathbf{C}^*) = \left[\tfrac{2}{5}(\mathbf{C}+\mathbf{C}^*)^{-1}_{ijij} - \tfrac{2}{15}(\mathbf{C}+\mathbf{C}^*)^{-1}_{iijj}\right]^{-1} - \mu_*,
\end{aligned} \tag{2}$$

$$\begin{aligned}
&\mathbf{C}^* = \mathbf{T}(k_*,\mu_*), \quad k_* = \frac{4}{3}\mu_0, \quad \mu_* = \mu_0\frac{9k_0+8\mu_0}{6k_0+12\mu_0},\\
&\bar{\mathbf{C}}^* = \mathbf{T}(\bar{k}_*,\bar{\mu}_*), \quad \bar{k}_* = \frac{4}{3}\bar{\mu}_0, \quad \bar{\mu}_* = \bar{\mu}_0\frac{9\bar{k}_0+8\bar{\mu}_0}{6\bar{k}_0+12\bar{\mu}_0},
\end{aligned} \tag{3}$$

$\mathbf{T}(k,\mu)$ is the isotropic fourth-rank tensor function with the components

$$T_{ijkl}(k,\mu) = (k - \tfrac{2}{3}\mu)\delta_{ij}\delta_{kl} + \mu(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}), \tag{4}$$

δ_{ij} is usual Kronecker symbol, conventional summation on repeating indices is assumed, and $(\mathbf{C}+\mathbf{C}^*)^{-1}_{ijkl}$ denote the components of the tensor $(\mathbf{C}+\mathbf{C}^*)^{-1}$. If the effective elasticity tensor $\mathbf{C}^e$ is taken definitely as isotropic, then it can be represented through the bulk (k_e) and shear (μ_e) moduli:

$$\mathbf{C}^e = \mathbf{T}(k_e,\mu_e). \tag{5}$$

Besides the base crystal elasticity tensor $\mathbf{C}$, the above bounds contain the free parameters k_0, μ_0 for the upper bounds and $\bar{k}_0$, $\bar{\mu}_0$ for the lower bounds. The parameters k_0, μ_0 for the upper bounds are restricted by

$$k_0 \geqslant k_V, \quad \mu_0 \geqslant \mu_V \tag{6}$$

and

$$U_K(\mathbf{C},k_0,\mu_0) \leqslant 0, \tag{7}$$

$$U_M(\mathbf{C},k_0,\mu_0) - \tfrac{1}{3}U_K(\mathbf{C},k_0,\mu_0) \leqslant 0, \tag{8}$$

where k_V and μ_V are Voigt's arithmetic average values

$$k_V = \tfrac{1}{9}C_{iijj}, \quad \mu_V = \tfrac{1}{10}C_{ijij} - \tfrac{1}{30}C_{iijj}. \tag{9}$$

The expressions of U_K and U_M are given in Appendix A ((A.1)–(A.4)). The best upper bounds are obtained when the free parameters k_0 and μ_0 restricted by (6)–(8) are chosen such as to make the upper bounds in (1) as small as possible.

The parameters $\bar{k}_0$, $\bar{\mu}_0$ for the lower bounds are restricted by

$$\bar{k}_0^{-1} \geqslant k_R^{-1}, \quad \bar{\mu}_0^{-1} \geqslant \mu_R^{-1}, \tag{10}$$

and

$$\bar{U}_K(\mathbf{C},\bar{k}_0,\bar{\mu}_0) \leqslant 0, \tag{11}$$

$$\bar{U}_M(\mathbf{C},\bar{k}_0,\bar{\mu}_0) - \tfrac{1}{3}\bar{U}_K(\mathbf{C},\bar{k}_0,\bar{\mu}_0) \leqslant 0, \tag{12}$$

where k_R and μ_R are Reuss' harmonic average values

$$k_R = [(\mathbf{C})^{-1}_{iijj}]^{-1}, \quad \mu_R = \left[\tfrac{2}{5}(\mathbf{C})^{-1}_{ijij} - \tfrac{2}{15}(\mathbf{C})^{-1}_{iijj}\right]^{-1}, \tag{13}$$

$\bar{U}_K$ and $\bar{U}_M$ have the same forms as U_K and U_M in (A.1) and (A.2) with $\bar{\mathbf{C}}^{-0}$, $\bar{\theta}$ and $\bar{\mathbf{D}}$ taking the places of $\mathbf{C}^{-0}$, θ and $\mathbf{D}$, respectively (see also (A.5)–(A.7) of Appendix A).

The best lower bounds are obtained when the free parameters $\bar{k}_0$, $\bar{\mu}_0$ restricted by (10)–(12) are chosen such as to make the lower bounds in (1) as large as possible.

One defines an interesting subclass of idealized spherical cell polycrystals, which are supposed to be composed exclusively from crystals of spherical forms and different sizes distributed randomly (Miller, 1969; Silnutzer, 1972; Zeller and Dederichs, 1973; Williemse and Caspers, 1979; Pham, 1996, 1997; Pham and Phan-Thien, 1998). The subclass is supposed to approximate practical equiaxed particulate aggregates. The bounds for them are especially simple, which have the structure (1)–(3) with the parameters k_0, μ_0 (for the upper bounds) and $\bar{k}_0$, $\bar{\mu}_0$ (for the lower bounds) coinciding with Voigt and Reuss averages, respectively

$$k_0 = k_{\mathrm{V}}, \quad \mu_0 = \mu_{\mathrm{V}}, \quad \bar{k}_0 = k_{\mathrm{R}}, \quad \bar{\mu}_0 = \mu_{\mathrm{R}}. \tag{14}$$

Hashin and Shtrikman (1962) bounds may also be expressed as (1)–(3) with k_0, μ_0, and $\bar{k}_0$, $\bar{\mu}_0$ being restricted by

$$\boldsymbol{\varepsilon} : (\mathbf{C} - \mathbf{C}^0) : \boldsymbol{\varepsilon} \leqslant 0, \quad \boldsymbol{\sigma} : [\mathbf{C}^{-1} - (\bar{\mathbf{C}}^0)^{-1}] : \boldsymbol{\sigma} \leqslant 0 \tag{15}$$

for all possible second rank symmetric tensors $\boldsymbol{\varepsilon}$ and $\boldsymbol{\sigma}$.

The self-consistent approximation k_s, μ_s for the aggregate moduli is the solution of the self-consistent equations

$$\begin{aligned} &k_s = P_k(\mathbf{C}, \mathbf{C}^{*s}), \quad \mu_s = P_\mu(\mathbf{C}, \mathbf{C}^{*s}), \\ &\mathbf{C}^{*s} = \mathbf{T}(k_{*s}, \mu_{*s}), \quad k_{*s} = \frac{4}{3}\mu_s, \quad \mu_{*s} = \mu_s \frac{9k_s + 8\mu_s}{6k_s + 12\mu_s}. \end{aligned} \tag{16}$$

3. The aggregate of trigonal crystals

The elastic tensor of trigonal crystals of classes $3m$, 32, $\bar{3}m$ in its base crystal reference is expressed through six elastic constants, which in the two-index notation are given as C_{11}, C_{12}, C_{13}, C_{14}, C_{33}, C_{44}. The correspondence between the usual fourth-rank elasticity tensor components C_{ijkl} and those in the two-index notation is

$$\begin{aligned} &C_{11} = C_{1111} = C_{2222}, \quad C_{33} = C_{3333}, \quad C_{44} = C_{1313} = C_{2323}, \\ &C_{13} = C_{1133} = C_{2233}, \quad C_{12} = C_{1122}, \quad C_{1212} = \tfrac{1}{2}(C_{11} - C_{12}), \\ &C_{14} = C_{1123} = -C_{2223} = C_{1312}. \end{aligned} \tag{17}$$

Voigt and Reuss averages from (8) and (13) have particular forms

$$\begin{aligned} &k_{\mathrm{V}} = \tfrac{1}{9}(2C_{11} + 2C_{12} + 4C_{13} + C_{33}), \\ &\mu_{\mathrm{V}} = \tfrac{1}{30}(7C_{11} - 5C_{12} - 4C_{13} + 2C_{33} + 12C_{44}), \\ &k_{\mathrm{R}} = \frac{(C_{11} + C_{12})C_{33} - 2C_{13}^2}{C_{11} + C_{12} - 4C_{13} + 2C_{33}}, \\ &\mu_{\mathrm{R}} = \frac{15}{2}\left[\frac{2C_{11} + 2C_{12} + 4C_{13} + C_{33}}{C_{33}(C_{11} + C_{12}) - 2C_{13}^2} + \frac{3C_{11} - 3C_{12} + 6C_{44}}{C_{44}(C_{11} - C_{12}) - 2C_{14}^2}\right]^{-1}. \end{aligned} \tag{18}$$

The property functions P_k and P_μ from (2) become

$$P_k(k_*, \mu_*) = \frac{(C_{11}^{+*} + C_{12}^{+*})C_{33}^{+*} - 2(C_{13}^{+*})^2}{C_{11}^{+*} + C_{12}^{+*} - 4C_{13}^{+*} + 2C_{33}^{+*}} - k_*, \tag{19}$$

$$P_\mu(k_*,\mu_*)=\frac{15}{2}\left[\frac{2C_{11}^{+*}+2C_{12}^{+*}+4C_{13}^{+*}+C_{33}^{+*}}{C_{33}^{+*}(C_{11}^{+*}+C_{12}^{+*})-2(C_{13}^{+*})^2}+\frac{3C_{11}^{+*}-3C_{12}^{+*}+6C_{44}^{+*}}{C_{44}^{+*}(C_{11}^{+*}-C_{12}^{+*})-2C_{14}^2}\right]^{-1}-\mu_*, \tag{20}$$

where

$$\begin{aligned} &C_{11}^{+*}=C_{11}+k_*+\tfrac{4}{3}\mu_*, \quad C_{33}^{+*}=C_{33}+k_*+\tfrac{4}{3}\mu_*, \quad C_{44}^{+*}=C_{44}+\mu_*,\\ &C_{12}^{+*}=C_{12}+k_*-\tfrac{2}{3}\mu_*, \quad C_{13}^{+*}=C_{13}+k_*-\tfrac{2}{3}\mu_*. \end{aligned} \tag{21}$$

The bounds for the specific spherical cell polycrystals are simple

$$k_s^{\mathrm{u}}\geqslant k_e\geqslant k_s^{\mathrm{l}}, \quad \mu_s^{\mathrm{u}}\geqslant\mu_e\geqslant\mu_s^{\mathrm{l}}, \tag{22}$$

where

$$\begin{aligned} &k_s^{\mathrm{u}}=P_k(k_*,\mu_*), \quad \mu_s^{\mathrm{u}}=P_\mu(k_*,\mu_*),\\ &k_s^{\mathrm{l}}=P_k(\bar{k}_*,\bar{\mu}_*), \quad \mu_s^{\mathrm{l}}=P_\mu(\bar{k}_*,\bar{\mu}_*), \end{aligned} \tag{23}$$

with k_*, μ_*, $\bar{k}_*$, $\bar{\mu}_*$ being determined by (3) and (14).

To derive the general shape-independent bounds for the elastic moduli, we must calculate the components D_{ijkl} from (A.4). These results are given in (B.1)–(B.3) of Appendix B. From (B.1) one can verify that

$$D_{11}+D_{12}+D_{13}=-\tfrac{1}{2}(D_{33}+2D_{31}), \quad D_{11}+D_{12}+D_{31}=-\tfrac{1}{2}(D_{33}+2D_{13}). \tag{24}$$

Substituting (B.1) into (A.1) and taking into account (24), after some algebra we obtain

$$U_K=\tfrac{1}{2}(D_{33}+2D_{31})^2Q(C_{ij}^{-0},k_0,\mu_0), \tag{25}$$

where

$$\begin{aligned} Q(C_{ij}^{-0},k_0,\mu_0)=&\frac{3\theta^2}{35}(3C_{11}^{-0}-C_{12}^{-0}+C_{33}^{-0}+4C_{44}^{-0})-\frac{2\theta}{35}(C_{11}^{-0}+C_{12}^{-0}+5C_{13}^{-0}+2C_{33}^{-0})\\ &+\left(\frac{4\theta^2}{35}-\frac{4\theta}{35}+\frac{1}{10}\right)\left(\frac{3}{2}C_{11}^{-0}-\frac{1}{2}C_{12}^{-0}+2C_{33}^{-0}+5C_{44}^{-0}\right)+\left(\frac{1}{10}-\frac{4\theta}{35}\right)\\ &\times\left(\frac{3}{2}C_{11}^{-0}-\frac{1}{2}C_{12}^{-0}+2C_{33}^{-0}-4C_{44}^{-0}\right)+\left(\frac{\theta^2}{75}+\frac{8\theta}{105}-\frac{1}{15}\right)(C_{11}^{-0}+C_{12}^{-0}-4C_{13}^{-0}+2C_{33}^{-0}), \end{aligned} \tag{26}$$

$$\begin{aligned} &C_{11}^{-0}=C_{11}-k_0-\tfrac{4}{3}\mu_0, \quad C_{33}^{-0}=C_{33}-k_0-\tfrac{4}{3}\mu_0, \quad C_{44}^{-0}=C_{44}-\mu_0,\\ &C_{12}^{-0}=C_{12}-k_0+\tfrac{2}{3}\mu_0, \quad C_{13}^{-0}=C_{13}-k_0+\tfrac{2}{3}\mu_0. \end{aligned} \tag{27}$$

The best shape-independent upper bound on the aggregate bulk modulus is

$$k_e\leqslant k^{\mathrm{u}}, \tag{28}$$

where

$$k^{\mathrm{u}}=\inf_{k_0,\mu_0}\{P_k(k_*,\mu_*)|k_0\geqslant k_{\mathrm{V}},\mu_0\geqslant\mu_{\mathrm{V}},Q(C_{ij}^{-0},k_0,\mu_0)\leqslant 0\}. \tag{29}$$

For numerical implementation of (29), we just increase k_0 and μ_0, respectively, from k_{V} and μ_{V} until we get $Q\leqslant 0$.

The best shape-independent upper bound on the shear modulus is

$$\mu_e\leqslant\mu^{\mathrm{u}}, \tag{30}$$

where

$$\mu^{\mathrm{u}} = \inf_{k_0,\mu_0} \left\{ P_\mu(k_*, \mu_*) | k_0 \geqslant k_{\mathrm{V}}, \mu_0 \geqslant \mu_{\mathrm{V}}, U_M - \tfrac{1}{3} U_K \leqslant 0 \right\}, \tag{31}$$

U_M is given by Eq. (B.4) of Appendix B.

Similarly, the best shape-independent lower bound on the bulk modulus is

$$k_e \geqslant k^{\mathrm{l}}, \tag{32}$$

where

$$k^{\mathrm{l}} = \sup_{\bar{k}_0,\bar{\mu}_0} \{ P_k(\bar{k}_*, \bar{\mu}_*) | \bar{k}_0^{-1} \geqslant k_{\mathrm{R}}^{-1}, \bar{\mu}_0^{-1} \geqslant \mu_{\mathrm{R}}^{-1}, \bar{Q}(\bar{C}_{ij}^{-0} \bar{k}_0, \bar{\mu}_0) \leqslant 0 \} \tag{33}$$

and the lower bound on the shear modulus is

$$\mu_e \geqslant \mu^{\mathrm{l}}, \tag{34}$$

where

$$\mu^{\mathrm{l}} = \sup_{\bar{k}_0,\bar{\mu}_0} \{ P_\mu(\bar{k}_*, \bar{\mu}_*) | \bar{k}_0^{-1} \geqslant k_{\mathrm{R}}^{-1}, \bar{\mu}_0^{-1} \geqslant \mu_{\mathrm{R}}^{-1}, \bar{U}_M - \tfrac{1}{3} \bar{U}_K \leqslant 0 \}, \tag{35}$$

$\bar{Q}$ and $\bar{U}_M$ have the same forms as Q from (26) and U_M from (B.4) with $\bar{\theta}$, $\bar{C}_{ij}^{-0}$ and $\bar{D}_{ij}$ (see (B.5)–(B.11) of Appendix B) taking the places of θ, C_{ij}^{-0} and D_{ij}, respectively.

Numerical results for the elastic moduli of the random aggregates of the trigonal crystals, the elastic constants of which are taken from Landolt-Börnstein (1979) (Table 1), are presented in Tables 2 and 3. The tabulated general shape-independent bounds (28)–(31) and (32)–(35), the bounds for specific spherical cell polycrystals (22) and (23), and the self-consistent values (16) are rounded to four significant digits. Hashin–Shtrikman bounds calculated in Watt and Peselnick (1980) are also included for a comparison. The relatively complicated general shape-independent bounds do not differ very much from the much simpler bounds for the specific spherical cell polycrystals (22), (23) and (14), which approximate practical equi-axed

Table 1
The elastic constants (in GPa) of trigonal crystals (classes $3m, 32, \bar{3}m$)

	C_{11}	C_{33}	C_{44}	C_{12}	C_{13}	C_{14}
$MgCO_3$	259	156	54.8	75.6	58.8	−19.0
$CaCO_3$	144.5	83.1	32.65	57.1	53.4	−20.5
Bi	63.7	38.2	11.23	24.9	24.7	7.17
Al_2O_3	496.8	498.1	147.4	163.6	110.9	−23.5
SiO_2	86.87	105.74	58.18	7.09	11.92	−18.04
$AlPO_4$	105	134	23.1	29.3	69.3	−12.7
Sb	101	44.8	39.6	31.4	27.0	22.1
Bi_2Te_3	68.5	47.7	27.4	21.8	27.0	13.2
CdI_2	43.1	22.5	5.5	20.4	8.9	0
CrO_3	374	362	159	148	175	−19
Fe_2O_3	242	228	85.3	54.9	15.7	−12.7
$FeBO_3$	445	305	95	145	140	20
PbI_2	27.7	20.2	6.2	9.6	11.3	3.0
$LiTaO_3$	230	276	95.9	42	79	−11
$KBrO_3$	43.1	23.6	16.6	14.4	15.5	−0.34
Se	18.6	76.1	14.8	7.3	25.2	5.6
Te	34.4	70.8	32.7	9.0	24.9	13.1
As	130	58.7	22.5	30.3	64.3	−3.7

Table 2
The upper and lower bounds on the polycrystalline elastic bulk modulus: k_{HS}^{u}, k_{HS}^{l}—Hashin–Shtrikman bounds; k^{u}, k^{l}—the shape-independent bounds; k_s^{u}, k_s^{l}—the bounds for spherical cell polycrystals; k_s—self-consistent value (in GPa); $S_k = (k^{u} - k^{l})/(k^{u} + k^{l})$—the scatter measure

	k_{HS}^{l}	k^{l}	k_s^{l}	k_s	k_s^{u}	k^{u}	k_{HS}^{u}	S_k
$MgCO_3$	113.2	113.8	113.9	114.0	114.1	114.1	114.5	0.0014
$CaCO_3$	74.4	74.85	74.93	75.14	75.35	75.35	75.9	0.0033
Bi	33.7	33.84	33.87	33.95	34.01	34.01	34.2	0.0025
Al_2O_3	251.1	251.1	251.1	251.1	251.1	251.1	251.1	0.00001
SiO_2	37.6	37.67	37.67	37.68	37.68	37.69	37.7	0.00021
$AlPO_4$		71.75	71.77	72.00	72.23	72.23		0.0033
Sb		43.03	43.17	43.49	43.82	43.82		0.0092
Bi_2Te_3		37.07	37.08	37.10	37.12	37.12		0.00064
CdI_2		18.70	18.73	18.79	18.86	18.86		0.0042
CrO_3		234.0	234.0	234.0	234.0	234.0		0
Fe_2O_3		97.77	97.77	97.78	97.78	97.78		0.00003
$FeBO_3$		223.7	223.8	223.8	223.9	223.9		0.00045
PbI_2		15.45	15.45	15.46	15.46	15.46		0.00035
$LiTaO_3$		124.8	124.8	124.8	124.8	124.8		0.00010
$KBrO_3$		21.61	21.66	21.69	21.70	21.70		0.0022
Se		13.84	13.84	15.30	16.96	17.58		0.12
Te		24.66	24.66	25.18	25.71	25.80		0.023
As		66.76	67.53	69.01	69.31	69.31		0.019

Table 3
The upper and lower bounds on the polycrystalline elastic shear modulus: $\mu_{HS}^{u}, \mu_{HS}^{l}$—Hashin–Shtrikman bounds; μ^{u}, μ^{l}—the shape-independent bounds; μ_s^{u}, μ_s^{l}—the bounds for spherical cell polycrystals; μ_s—self-consistent value (in GPa); $S_\mu = (\mu^{u} - \mu^{l})/(\mu^{u} + \mu^{l})$—the scatter measure

	μ_{HS}^{l}	μ^{l}	μ_s^{l}	μ_s	μ_s^{u}	μ^{u}	μ_{HS}^{u}	S_μ
$MgCO_3$	67.1	67.78	67.78	67.91	68.03	68.04	68.5	0.0019
$CaCO_3$	29.1	29.93	29.93	30.28	30.62	30.64	31.7	0.012
Bi	12.0	12.37	12.37	12.49	12.60	12.61	13.0	0.0096
Al_2O_3	163.2	163.4	163.4	163.4	163.5	163.5	163.7	0.00013
SiO_2	43.5	44.01	44.01	44.11	44.22	44.26	44.9	0.0028
$AlPO_4$		24.96	24.96	25.14	25.32	25.32		0.0072
Sb		26.11	26.12	26.63	27.21	27.25		0.021
Bi_2Te_3		19.26	19.26	19.43	19.63	19.65		0.010
CdI_2		8.448	8.448	8.472	8.498	8.498		0.0029
CrO_3		123.1	123.1	123.1	123.2	123.2		0.00045
Fe_2O_3		93.08	93.09	93.10	93.11	93.11		0.00012
$FeBO_3$		115.0	115.0	115.1	115.1	115.1		0.00069
PbI_2		6.532	6.532	6.554	6.577	6.578		0.0035
$LiTaO_3$		92.06	92.06	92.07	92.07	92.07		0.00006
$KBrO_3$		13.07	13.14	13.17	13.18	13.18		0.0042
Se		6.722	6.748	7.250	7.817	7.817		0.075
Te		14.12	14.15	14.84	15.61	15.66		0.052
As		18.69	19.81	22.91	23.73	23.73		0.12

particulate aggregates. Hence, the latter may give good estimation of the scatter ranges for many practical polycrystalline aggregates and can be recommended for practical use. Note that they are even simpler than the less tight Hashin-Shtrikman bounds.

4. The uncertainty and asymptotic estimates

As stated in Section 1, there are no mathematical or experimental proofs of the conventional assumption that the effective moduli of a particular random polycrystalline material should be unique. On the contrary, because of the irregular microgeometry, the effective properties of a random polycrystalline material may be not unique, and two different representative elements (in large limit compared to the sizes of constituent grains) of the same polycrystalline material may have slightly different effective properties (because they do not have identical microgeometry). We presume our bounds provide these possible scatter ranges of the effective moduli. Once the effective moduli of a random polycrystal are not unique, the macroscopic homogeneity and isotropy hypotheses for it are not exact anymore and can be considered only as approximate. So in this sense, at least as a conservative measure, we should abandon the precise isotropy statement (5) and come to the general inequalities (1) where $\mathbf{C}^e$ can be slightly anisotropic (of all possible kinds) as allowed by the bounds. Hence, the shape-independent bounds (28), (30), (32) and (34) should be understood as

$$\boldsymbol{\varepsilon} : \mathbf{T}(k^u, \mu^u) : \boldsymbol{\varepsilon} \geqslant \boldsymbol{\varepsilon} : \mathbf{C}^e : \boldsymbol{\varepsilon} \geqslant \boldsymbol{\varepsilon} : \mathbf{T}(k^l, \mu^l) : \boldsymbol{\varepsilon} \quad (\forall \text{ symmetric } \boldsymbol{\varepsilon}). \tag{36}$$

However the particular expressions of the upper and lower bounds k^u, μ^u, k^l, μ^l themselves have been derived using mathematical expressions of statistical isotropy and symmetry hypotheses, which are supposed to be not exact but approximate. This means the bounds are not rigorous and could be violated by the effective moduli. Still, they can be interpreted in "extended asymptotical sense" as follows.

As the size of the scatter range of the bounds (36) we take

$$\begin{aligned} &S = \max\{S_k, S_\mu\}, \\ &S_k = (k^u - k^l)/(k^u + k^l), \quad S_\mu = (\mu^u - \mu^l)/(\mu^u + \mu^l). \end{aligned} \tag{37}$$

The respective size of the scatter range of the respective bounds for specific spherical cell polycrystals is designated as S_s.

It appears that the scatter measures of our bounds are small for considered polycrystalline materials, in particular S, $S_s \ll 1$. We have known that, in asymptotic sense, the bounds for spherical cell polycrystals are third order in the base crystal elasticity anisotropy contrast for an expansion around a homogeneity (with the respective range size S_s), while the Voigt–Reuss–Hill bounds are first order (hence, with the range size equivalent to $S_s^{1/3}$), and Hashin–Shtrikman bounds are second order (with the measure equivalent to $S_s^{2/3}$). The shape-independent bounds (36) are partly third order (with the measure $S \geqslant S_s$)—but close to S_s as we have seen in the previous section.

Because the statistical isotropy and other hypotheses used for derivation of the bounds (36) may be not exact, the bounds may be considered only as approximate in asymptotic sense as follows. Presume the accuracy of the hypotheses is about the amount S, as suggested by the bounds. The lowest order terms in the expressions of the upper and lower bounds, where the isotropy hypothesis has been applied to evaluate, are the second order ones (equivalent to $S_s^{2/3}$), in particular the terms involving the approximations (3) of Pham (1997). This leads subsequently to the possible errors of about $S \cdot S_s^{2/3}$ for the expressions of the shape-independent bounds (or about fifth order $S_s \cdot S_s^{2/3} = S_s^{5/3}$ in the spherical cell polycrystal case). Say, the effective moduli may be even larger (smaller) than the derived upper (lower) bounds by these small amounts. Then we have the relative possible error $r = S \cdot S_s^{2/3}/S = S_s^{2/3}$ for the derived scatter range S (the same error expression for S_s). Thus the bounds may give reliable prediction of the uncertainty interval S (and S_s) only under the condition that this relative error r is small:

$$r = S_s^{2/3} \ll 1. \tag{38}$$

Roughly speaking the effective properties may have values higher than the upper bounds, or lower than the lower bounds by amounts small compared to the distances between the bounds if r is small. The bounds become not rigorous mathematically and should be understood in this extended asymptotic sense.

As S, S_s increase, r increases correspondingly toward 1, so the magnitudes of the errors may become comparable to the intervals between the bounds, invalidating the practical significance of the bounds. In other words, the bounds would be useful only when they are sufficiently narrow, while when they are wide, the effective moduli may correspondingly fall far outside if one does not presume, in addition, that the real scatter range should be much smaller than the interval between the obtained bounds. In that case the bounds become poor predictor and may have only some mathematical, not practical, value! The scatter measures S_k, S_μ calculated for the particular crystals in Tables 2 and 3 are rounded to five decimal places, or two significant figures. They appear to be rather small. For most of them $r \leqslant S^{2/3}$ is only about a few thousandths, so the obtained numerical results can be considered as reliable in predicting scatter ranges.

One may suggest that narrower bounds could be derived if higher-order correlation information about the aggregate geometry is incorporated. However, like the effective moduli of a random polycrystal are not unique, the high order correlation functions may also be not unique and can only be determined with some uncertainty, while the amounts of these uncertainties may increase for higher order correlation information. If the uncertainties of the lower order statistical information, as the isotropy and homogeneity hypotheses, should be indeed as large as comparable to the scatter intervals predicted by our bounds, then the higher order correlation functions with corresponding (increasing) uncertainties may add little or nothing to improve the bounds. Alternatively, if the uncertainties of observed macroscopic moduli of a random polycrystal should indeed be much smaller than the intervals predicted by our bounds, then the accuracy of the isotropy and homogeneity hypotheses should be higher than that given by our bounds (36), while the accuracy of our bounds (in mathematical sense) should be better in the sense that the derived bounds may be violated by amounts much smaller than those indicated above. However the bounds then become of less use because they predict some too wide intervals, not the good estimation of real uncertainties. In that case, we need to incorporate new realistic hypotheses to improve the bounds accordingly and drastically. At present we do not see any such mathematical possibility. The derived bounds are about third order, and our and other authors' works show that one cannot go further than third order bounds without specifying shape and packing information about the microgeometry of a random aggregate (beside the random hypotheses), but such information is unlikely to be definite, even in principle, for a real-world random polycrystal with irregular microgeometry, not saying about our ability to find such information. Precise experiments should provide an answer to this question. In this respect we may cite the experimental data collected in Warra et al. (1977), Kröner (1980) to check if the measured macroscopic elastic moduli of random polycrystalline materials should be concentrated toward the self-consistent values. Instead, the authors observe that the macroscopic moduli scatter almost uniformly over an interval comparable to that of the third order bounds—the fact agrees qualitatively with the prediction of our shape-independent nearly third order bounds, though it does not provide direct verification of our bounds, which require experimental data of many samples for every particular polycrystalline material, not the average value. Our calculated bounds for a number of polycrystals, including those collected in Tables 2 and 3 of this paper, indicate that one may determine the macroscopic elastic moduli of most materials with the accuracy only up to from 2 to 4 significant digits (measured values with higher number of digits might be subjected to fluctuations from sample to sample as allowed by the bounds). Note that tabulated elastic moduli of technical polycrystalline materials are often given only with very few significant digits. Apart from possible impurities, technological and measurement factors, the fluctuations caused by the "uncertainty of the random nature" described in this paper might play a major role.

One can also think of some numerical experiments: e.c. Voronoi tessellation of space with respect to a set of points thrown randomly and then assigning each cell a random orientation of the base crystal. This model may be used to test the uniqueness of the elastic moduli and the possible scatter ranges for a random polycrystal. We expect the calculated effective moduli would scatter (fluctuate from one realization to another) as predicted by the bounds. However the solution of the elastic equilibrium equations on huge representative elements with irregular microgeometry, together with high accuracy requirements, makes the

problem a formidable task. At present we think direct experimental verifications are more feasible. It should be noted in addition that some idealistic random cell models have been constructed, which have the effective properties covering large proportions of the intervals within our bounds (Pham, 1998; Pham and Phan-Thien, 1998).

In conclusion, our view is that the effective elastic moduli of a random polycrystalline material are not unique, the homogeneity and isotropy hypotheses for it are not exact, and our bounds may provide the measure of that uncertainty, which should be understood in the sense of (36), asymptotically with relative accuracy (38). The bounds and the hypotheses are interrelated once the bounds are expected to predict the observed uncertainty, hence also the accuracy of the hypotheses. The uncertainty puts limits on the accuracy, with which the macroscopic elastic constants of a random polycrystalline material could be determined theoretically or experimentally. The boundary-value elastic equilibrium problems for technical random polycrystalline materials cannot be solved with arbitrary high accuracy even theoretically, but with that limited by the uncertainty of the coefficients (the effective elastic moduli) of the respective differential equations. Furthermore an elastic wave transmitting through such a macroscopically slightly inhomogeneous medium, even in the long wave limit, may be scattered and attenuated, though such effects appear to be weak. These qualitative observations are expected to apply to any randomly inhomogeneous continuum. Roughly speaking, if it is randomly inhomogeneous on microscopic level, it may be slightly inhomogeneous on the macroscopic scale (but without clearly defined sizes of "macroscopic inhomogeneities")—in difference with periodic structures, where macroscopic properties are proved to be unique and macroscopic homogeneity is guaranteed. Direct and high accuracy experiments are needed to check our theoretical results for them to be of possible practical significance.

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Appendix A

Some additional formulae for the general bounds:

$$U_K = C^{-0}_{ijij}D_{klpp}D_{klqq}\frac{\theta^2}{35} - C^{-0}_{iikk}D_{jjpp}D_{llqq}\frac{2\theta^2}{525} - C^{-0}_{iikl}D_{kjpp}D_{ljqq}\frac{2\theta}{35} + C^{-0}_{ijik}D_{jlpp}D_{klqq}\left(\frac{4\theta^2}{35} - \frac{4\theta}{35} + \frac{1}{10}\right) - C^{-0}_{ijik}D_{kjpp}D_{llqq}\frac{2\theta}{35} + C^{-0}_{ijkl}D_{ijpp}D_{klqq}\left(\frac{\theta^2}{75} + \frac{8\theta}{105} - \frac{1}{15}\right) + C^{-0}_{ijkl}D_{ikpp}D_{ljqq}\left(\frac{1}{10} - \frac{4\theta}{35}\right) + C^{-0}_{ijkk}D_{ijpp}D_{llqq}\left(\frac{4\theta}{105} - \frac{8\theta^2}{525}\right), \tag{A.1}$$

$$U_M = C^{-0}_{ijij}D_{klpq}D_{klpq}\frac{\theta^2}{35} - C^{-0}_{iikk}D_{jjpq}D_{llpq}\frac{2\theta^2}{525} - C^{-0}_{iikl}D_{kjpq}D_{ljpq}\frac{2\theta}{35} + C^{-0}_{ijik}D_{jlpq}D_{klpq}\left(\frac{4\theta^2}{35} - \frac{4\theta}{35} + \frac{1}{10}\right) - C^{-0}_{ijik}D_{kjpq}D_{llpq}\frac{2\theta}{35} + C^{-0}_{ijkl}D_{ijpq}D_{klpq}\left(\frac{\theta^2}{75} + \frac{8\theta}{105} - \frac{1}{15}\right) + C^{-0}_{ijkl}D_{ikpq}D_{ljpq}\left(\frac{1}{10} - \frac{4\theta}{35}\right) + C^{-0}_{ijkk}D_{ijpq}D_{llpq}\left(\frac{4\theta}{105} - \frac{8\theta^2}{525}\right), \tag{A.2}$$

$$\mathbf{C}^{-0} = \mathbf{C} - \mathbf{C}^0, \quad \mathbf{C}^0 = \mathbf{T}(k_0, \mu_0), \quad \theta = \frac{3k_0 + \mu_0}{3k_0 + 4\mu_0}, \tag{A.3}$$

$$D_{ijkl} = \tfrac{1}{2}(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - \delta_{kl}(k^{+*} - \tfrac{2}{3}\mu^{+*})(\mathbf{C} + \mathbf{C}^*)^{-1}_{ijnn} - 2\mu^{+*}(\mathbf{C} + \mathbf{C}^*)^{-1}_{ijkl},$$
$$k^{+*} = [(\mathbf{C} + \mathbf{C}^*)^{-1}_{iijj}]^{-1}, \quad \mu^{+*} = \left[\tfrac{2}{5}(\mathbf{C} + \mathbf{C}^*)^{-1}_{ijij} - \tfrac{2}{15}(\mathbf{C} + \mathbf{C}^*)^{-1}_{iijj}\right]^{-1}. \tag{A.4}$$

$\bar{U}_K$ and $\bar{U}_M$ have the same forms as U_K and U_M with $\bar{\mathbf{C}}^{-0}$, $\bar{\theta}$ and $\bar{\mathbf{D}}$ taking the places of $\mathbf{C}^{-0}$, θ and $\mathbf{D}$, respectively:

$$\bar{\mathbf{C}}^{-0} = \bar{\mathbf{C}}^0 : [\mathbf{C}^{-1} - (\bar{\mathbf{C}}^0)^{-1}] : \bar{\mathbf{C}}^0, \quad \bar{\mathbf{C}}^0 = \mathbf{T}(\bar{k}_0, \bar{\mu}_0), \quad \bar{\theta} = \frac{3\bar{k}_0 + \bar{\mu}_0}{3\bar{k}_0 + 4\bar{\mu}_0}, \tag{A.5}$$

$$\begin{aligned}\bar{D}_{ijkl} = {} & \left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\delta_{ij}\delta_{kl} + \bar{\mu}_0(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk}) - \left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\delta_{ij}\delta_{kl}\left(\bar{k}^{+*} - \tfrac{2}{3}\bar{\mu}^{+*}\right)[\mathbf{C}^{-1} + (\bar{\mathbf{C}}^*)^{-1}]^{-1}_{ppqq} \\ & - 2\bar{\mu}_0\delta_{kl}\left(\bar{k}^{+*} - \tfrac{2}{3}\bar{\mu}^{+*}\right)[\mathbf{C}^{-1} + (\bar{\mathbf{C}}^*)^{-1}]^{-1}_{ijqq} - 2\bar{\mu}^{+*}\left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\delta_{ij}[\mathbf{C}^{-1} + (\bar{\mathbf{C}}^*)^{-1}]^{-1}_{ppkl} \\ & - 4\bar{\mu}_0\bar{\mu}^{+*}[\mathbf{C}^{-1} + (\bar{\mathbf{C}}^*)^{-1}]^{-1}_{ijkl},\end{aligned} \tag{A.6}$$

$$\bar{k}^{+*} = ([\mathbf{C}^{-1} + (\bar{\mathbf{C}}^*)^{-1}]^{-1}_{iijj})^{-1},$$
$$\bar{\mu}^{+*} = \left(\tfrac{2}{5}[\mathbf{C}^{-1} + (\bar{\mathbf{C}}^*)^{-1}]^{-1}_{ijij} - \tfrac{2}{15}[\mathbf{C}^{-1} + (\bar{\mathbf{C}}^*)^{-1}]^{-1}_{iijj}\right)^{-1}. \tag{A.7}$$

Appendix B

Additional formulae for the bounds on the aggregate of trigonal crystals (classes $3m, 32, \bar{3}m$). For the upper bounds we have:

$$\begin{aligned}
&D_{1111} = D_{2222} = D_{11} = 1 - \left(k^{+*} - \tfrac{2}{3}\mu^{+*}\right)(S^{+*}_{11} + S^{+*}_{12} + S^{+*}_{13}) - 2\mu^{+*}S^{+*}_{11}, \\
&D_{1122} = D_{2211} = D_{12} = -\left(k^{+*} - \tfrac{2}{3}\mu^{+*}\right)(S^{+*}_{11} + S^{+*}_{12} + S^{+*}_{13}) - 2\mu^{+*}S^{+*}_{12}, \\
&D_{1133} = D_{2233} = D_{13} = -\left(k^{+*} - \tfrac{2}{3}\mu^{+*}\right)(S^{+*}_{11} + S^{+*}_{12} + S^{+*}_{13}) - 2\mu^{+*}S^{+*}_{13}, \\
&D_{3311} = D_{3322} = D_{31} = -\left(k^{+*} - \tfrac{2}{3}\mu^{+*}\right)(2S^{+*}_{13} + S^{+*}_{33}) - 2\mu^{+*}S^{+*}_{13}, \\
&D_{3333} = D_{33} = 1 - \left(k^{+*} - \tfrac{2}{3}\mu^{+*}\right)(2S^{+*}_{13} + S^{+*}_{33}) - 2\mu^{+*}S^{+*}_{33}, \\
&D_{2323} = D_{1313} = D_{44} = \tfrac{1}{2} - 2\mu^{+*}S^{+*}_{44}, \quad D_{1212} = D_{66} = \tfrac{1}{2} - \mu^{+*}(S^{+*}_{11} - S^{+*}_{12}), \\
&D_{1123} = D_{2311} = D_{3112} = D_{1231} = D_{14} = -2\mu^{+*}S^{+*}_{14}, \\
&D_{2223} = D_{2322} = D_{24} = -2\mu^{+*}S^{+*}_{14} = -D_{14},
\end{aligned} \tag{B.1}$$

where

$$k^{+*} = P_k(k_*, \mu_*) + k_*, \quad \mu^{+*} = P_\mu(k_*, \mu_*) + \mu_*, \tag{B.2}$$

$$\begin{aligned}
S^{+*}_{11} &= \frac{1}{2}\left[\frac{C^{+*}_{33}}{C^{+*}_{33}(C^{+*}_{11} + C^{+*}_{12}) - 2(C^{+*}_{13})^2} + \frac{C^{+*}_{44}}{C^{+*}_{44}(C^{+*}_{11} - C^{+*}_{12}) - 2C^2_{14}}\right], \\
S^{+*}_{12} &= \frac{1}{2}\left[\frac{C^{+*}_{33}}{C^{+*}_{33}(C^{+*}_{11} + C^{+*}_{12}) - 2(C^{+*}_{13})^2} - \frac{C^{+*}_{44}}{C^{+*}_{44}(C^{+*}_{11} - C^{+*}_{12}) - 2C^2_{14}}\right], \\
S^{+*}_{13} &= \frac{-C^{+*}_{13}}{(C^{+*}_{11} + C^{+*}_{12})C^{+*}_{33} - 2(C^{+*}_{13})^2}, \quad S^{+*}_{33} = \frac{C^{+*}_{11} + C^{+*}_{12}}{(C^{+*}_{11} + C^{+*}_{12})C^{+*}_{33} - 2(C^{+*}_{13})^2}, \\
S^{+*}_{44} &= \frac{(C^{+*}_{11} - C^{+*}_{12})/4}{(C^{+*}_{11} - C^{+*}_{12})C^{+*}_{44} - 2C^2_{14}}, \quad S^{+*}_{14} = \frac{-C_{14}/2}{(C^{+*}_{11} - C^{+*}_{12})C^{+*}_{44} - 2C^2_{14}},
\end{aligned} \tag{B.3}$$

$$
\begin{aligned}
U_M = {} & \frac{\theta^2}{35}(3C_{11}^{-0} - C_{12}^{-0} + C_{33}^{-0} + 4C_{44}^{-0})(3D_{11}^2 + D_{33}^2 + 3D_{12}^2 + 2D_{13}^2 + 2D_{31}^2 - 2D_{11}D_{12} + 8D_{44}^2 + 16D_{14}^2) \\
& - \frac{2\theta^2}{525}(2C_{11}^{-0} + C_{33}^{-0} + 2C_{12}^{-0} + 4C_{13}^{-0})\frac{3}{2}(D_{33} + 2D_{13})^2 - \frac{2\theta}{35}[(C_{11}^{-0} + C_{12}^{-0} + C_{13}^{-0}) \\
& \times (3D_{11}^2 + 3D_{12}^2 + 2D_{13}^2 + 4D_{44}^2 - 2D_{11}D_{12} + 10D_{14}^2) + (C_{33}^{-0} + 2C_{13}^{-0})(D_{33}^2 + 2D_{31}^2 + 4D_{44}^2 + 4D_{14}^2)] \\
& + \left(\frac{4\theta^2}{35} - \frac{4\theta}{35} + \frac{1}{10}\right)\left[\frac{3}{2}(C_{11}^{-0} - \frac{1}{2}C_{12}^{-0} + C_{44}^{-0})(3D_{11}^2 + 3D_{12}^2 - 2D_{11}D_{12} + 4D_{44}^2 + 2D_{13}^2 + 10D_{14}^2)\right. \\
& \left. + (C_{33}^{-0} + 2C_{44}^{-0})(D_{33}^2 + 2D_{31}^2 + 4D_{44}^2 + 4D_{14}^2)\right] - \frac{2\theta}{35}\left[\left(\frac{3}{2}C_{11}^{-0} - \frac{1}{2}C_{12}^{-0} + C_{44}^{-0}\right)(2D_{13} - D_{11} - D_{12})\right. \\
& \left. \times (2D_{13} + D_{33}) + (C_{33}^{-0} + 2C_{44}^{-0})(D_{33} - D_{31})(D_{33} + 2D_{13})\right] + \left(\frac{\theta^2}{75} + \frac{8\theta}{105} - \frac{1}{15}\right)[C_{11}^{-0}(3D_{11}^2 + 3D_{12}^2 \\
& + 2D_{13}^2 + 8D_{14}^2 - 2D_{11}D_{12}) + C_{33}^{-0}(D_{33}^2 + 2D_{31}^2) + C_{12}^{-0}(6D_{11}D_{12} + 2D_{13}^2 - 8D_{14}^2 - 2D_{11}^2 - 2D_{12}^2) \\
& + 4C_{13}^{-0}(D_{11}D_{31} + D_{12}D_{31} + D_{13}D_{33}) + 16C_{44}^{-0}(D_{44}^2 + D_{14}^2) + 16C_{14}^{-0}D_{14}^2(2D_{44} + D_{11} - D_{12})] \\
& + \left(\frac{1}{10} - \frac{4\theta}{35}\right)\left[C_{11}^{-0}\left(\frac{5}{2}D_{11}^2 + \frac{5}{2}D_{12}^2 + 3D_{13}^2 + 4D_{14}^2 + D_{11}D_{12}\right) + C_{33}^{-0}(D_{33}^2 + 2D_{31}^2) + 8C_{13}^{-0}(D_{44}^2 + D_{14}^2)\right. \\
& \left. + C_{12}^{-0}\left(4D_{14}^2 + \frac{1}{2}D_{11}^2 + \frac{1}{2}D_{12}^2 - D_{13}^2 - 3D_{11}D_{12}\right) + 4C_{44}^{-0}(2D_{44}^2 + 2D_{14}^2 + D_{11}D_{31} + D_{12}D_{31} + D_{13}D_{33})\right. \\
& \left. + 8C_{14}^{-0}D_{14}(D_{11} - D_{12} + 4D_{44})\right] + \left(\frac{4\theta}{105} - \frac{8\theta^2}{525}\right)[(C_{11}^{-0} + C_{12}^{-0} + C_{13}^{-0})(2D_{13} - D_{11} - D_{12})(D_{33} + 2D_{13}) \\
& + (C_{33}^{-0} + 2C_{31}^{-0})(D_{33} - D_{31})(D_{33} + 2D_{13})].
\end{aligned}
\tag{B.4}
$$

For the lower bounds we have:

$$
\begin{aligned}
\bar{D}_{11} = {} & -2\left[\bar{\mu}_0\left(\bar{k}^{+*} - \tfrac{2}{3}\bar{\mu}^{+*}\right) + \bar{\mu}^{+*}\left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\right](\bar{C}_{11}^{+*} + \bar{C}_{12}^{+*} + \bar{C}_{13}^{+*}) + 2\bar{\mu}_0 + \left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\tfrac{2}{3}\bar{\mu}^{+*} \\
& \Big/\bar{k}^{+*} - 4\bar{\mu}_0\bar{\mu}^{+*}\bar{C}_{11}^{+*}, \\
\bar{D}_{12} = {} & -2\left[\bar{\mu}_0\left(\bar{k}^{+*} - \tfrac{2}{3}\bar{\mu}^{+*}\right) + \bar{\mu}^{+*}\left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\right](\bar{C}_{11}^{+*} + \bar{C}_{12}^{+*} + \bar{C}_{13}^{+*}) + \left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\tfrac{2}{3}\bar{\mu}^{+*} \\
& \Big/\bar{k}^{+*} - 4\bar{\mu}_0\bar{\mu}^{+*}\bar{C}_{12}^{+*}, \\
\bar{D}_{33} = {} & -2\left[\bar{\mu}_0\left(\bar{k}^{+*} - \tfrac{2}{3}\bar{\mu}^{+*}\right) + \bar{\mu}^{+*}\left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\right](\bar{C}_{33}^{+*} + 2\bar{C}_{13}^{+*}) + 2\bar{\mu}_0 + \left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\tfrac{2}{3}\bar{\mu}^{+*} \\
& \Big/\bar{k}^{+*} - 4\bar{\mu}_0\bar{\mu}^{+*}\bar{C}_{33}^{+*}, \\
\bar{D}_{13} = {} & -2\bar{\mu}_0\left(\bar{k}^{+*} - \tfrac{2}{3}\bar{\mu}^{+*}\right)(\bar{C}_{11}^{+*} + \bar{C}_{12}^{+*} + \bar{C}_{13}^{+*}) - 4\bar{\mu}_0\bar{\mu}^{+*}\bar{C}_{13}^{+*} - 2\left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\bar{\mu}^{+*}(\bar{C}_{33}^{+*} + 2\bar{C}_{13}^{+*}) \\
& + \left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\tfrac{2}{3}\bar{\mu}^{+*}\Big/\bar{k}^{+*}, \\
\bar{D}_{31} = {} & -2\bar{\mu}_0\left(\bar{k}^{+*} - \tfrac{2}{3}\bar{\mu}^{+*}\right)(\bar{C}_{33}^{+*} + 2\bar{C}_{13}^{+*}) - 4\bar{\mu}_0\bar{\mu}^{+*}\bar{C}_{13}^{+*} - 2\left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\bar{\mu}^{+*}(\bar{C}_{11}^{+*} + \bar{C}_{12}^{+*} + \bar{C}_{13}^{+*}) \\
& + \left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)\tfrac{2}{3}\bar{\mu}^{+*}\Big/\bar{k}^{+*}, \\
\bar{D}_{44} = {} & \bar{\mu}_0 - 4\bar{\mu}_0\bar{\mu}^{+*}\bar{C}_{44}^{+*}, \quad \bar{D}_{14} = -4\bar{\mu}_0\bar{\mu}^{+*}\bar{C}_{14}^{+*},
\end{aligned}
\tag{B.5}
$$

where

$$\bar{k}^{+*} = (2\bar{C}_{11}^{+*} + 2\bar{C}_{12}^{+*} + 4\bar{C}_{13}^{+*} + \bar{C}_{33}^{+*})^{-1},$$
$$\bar{\mu}^{+*} = \frac{15}{2}(7\bar{C}_{11}^{+*} - 5\bar{C}_{12}^{+*} - 4\bar{C}_{13}^{+*} + 2\bar{C}_{33}^{+*} + 12\bar{C}_{44}^{+*})^{-1}, \tag{B.6}$$

$$\bar{C}_{11}^{+*} = \frac{1}{2}\left[\frac{\bar{S}_{33}^{+*}}{\bar{S}_{33}^{+*}(\bar{S}_{11}^{+*} + \bar{S}_{12}^{+*}) - 2(\bar{S}_{13}^{+*})^2} + \frac{\bar{S}_{44}^{+*}}{\bar{S}_{44}^{+*}(\bar{S}_{11}^{+*} - \bar{S}_{12}^{+*}) - 2\bar{S}_{14}^2}\right],$$
$$\bar{C}_{12}^{+*} = \frac{1}{2}\left[\frac{\bar{S}_{33}^{+*}}{\bar{S}_{33}^{+*}(\bar{S}_{11}^{+*} + \bar{S}_{12}^{+*}) - 2(\bar{S}_{13}^{+*})^2} - \frac{\bar{S}_{44}^{+*}}{\bar{S}_{44}^{+*}(\bar{S}_{11}^{+*} - \bar{S}_{12}^{+*}) - 2\bar{S}_{14}^2}\right],$$
$$\bar{C}_{13}^{+*} = \frac{-\bar{S}_{13}^{+*}}{(\bar{S}_{11}^{+*} + \bar{S}_{12}^{+*})\bar{S}_{33}^{+*} - 2(\bar{S}_{13}^{+*})^2}, \quad \bar{C}_{33}^{+*} = \frac{\bar{S}_{11}^{+*} + \bar{S}_{12}^{+*}}{(\bar{S}_{11}^{+*} + \bar{S}_{12}^{+*})\bar{S}_{33}^{+*} - 2(\bar{S}_{13}^{+*})^2}, \tag{B.7}$$
$$\bar{C}_{44}^{+*} = \frac{(\bar{S}_{11}^{+*} - \bar{S}_{12}^{+*})/4}{(\bar{S}_{11}^{+*} - \bar{S}_{12}^{+*})\bar{S}_{44}^{+*} - 2\bar{S}_{14}^2}, \quad \bar{C}_{14}^{+*} = \frac{-\bar{S}_{14}/2}{(\bar{S}_{11}^{+*} - \bar{S}_{12}^{+*})\bar{S}_{44}^{+*} - 2\bar{S}_{14}^2},$$

$$\bar{S}_{11}^{+*} = S_{11} + \frac{1}{9\bar{k}_*} + \frac{1}{3\bar{\mu}_*}, \quad \bar{S}_{33}^{+*} = S_{33} + \frac{1}{9\bar{k}_*} + \frac{1}{3\bar{\mu}_*}, \quad \bar{S}_{44}^{+*} = S_{44} + \frac{1}{4\bar{\mu}_*},$$
$$\bar{S}_{12}^{+*} = S_{12} + \frac{1}{9\bar{k}_*} - \frac{1}{6\bar{\mu}_*}, \quad \bar{S}_{13}^{+*} = S_{13} + \frac{1}{9\bar{k}_*} - \frac{1}{6\bar{\mu}_*}, \tag{B.8}$$

$$S_{11} = \frac{1}{2}\left[\frac{C_{33}}{C_{33}(C_{11} + C_{12}) - 2C_{13}^2} + \frac{C_{44}}{C_{44}(C_{11} - C_{12}) - 2C_{14}^2}\right],$$
$$S_{12} = \frac{1}{2}\left[\frac{C_{33}}{C_{33}(C_{11} + C_{12}) - 2C_{13}^2} - \frac{C_{44}}{C_{44}(C_{11} - C_{12}) - 2C_{14}^2}\right],$$
$$S_{13} = \frac{-C_{13}}{(C_{11} + C_{12})C_{33} - 2C_{13}^2}, \quad S_{33} = \frac{C_{11} + C_{12}}{(C_{11} + C_{12})C_{33} - 2C_{13}^2}, \tag{B.9}$$
$$S_{44} = \frac{(C_{11} - C_{12})/4}{(C_{11} - C_{12})C_{44} - 2C_{14}^2}, \quad S_{14} = \frac{-C_{14}/2}{(C_{11} - C_{12})C_{44} - 2C_{14}^2},$$

$$\bar{C}_{11}^{-0} = \left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)^2(2S_{11} + 2S_{12} + 4S_{13} + S_{33}) + 4\bar{\mu}_0\left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)(S_{11} + S_{12} + S_{13}) + 4\bar{\mu}_0^2 S_{11} - \bar{k}_0 - \tfrac{4}{3}\bar{\mu}_0,$$
$$\bar{C}_{12}^{-0} = \left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)^2(2S_{11} + 2S_{12} + 4S_{13} + S_{33}) + 4\bar{\mu}_0\left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)(S_{11} + S_{12} + S_{13}) + 4\bar{\mu}_0^2 S_{12} - \bar{k}_0 + \tfrac{2}{3}\bar{\mu}_0,$$
$$\bar{C}_{13}^{-0} = \left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)^2(2S_{11} + 2S_{12} + 4S_{13} + S_{33}) + 2\bar{\mu}_0\left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)(S_{11} + S_{12} + 3S_{13} + S_{33}) + 4\bar{\mu}_0^2 S_{13} - \bar{k}_0 + \tfrac{2}{3}\bar{\mu}_0,$$
$$\bar{C}_{33}^{-0} = \left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)^2(2S_{11} + 2S_{12} + 4S_{13} + S_{33}) + 4\bar{\mu}_0\left(\bar{k}_0 - \tfrac{2}{3}\bar{\mu}_0\right)(2S_{13} + S_{33}) + 4\bar{\mu}_0^2 S_{33} - \bar{k}_0 - \tfrac{4}{3}\bar{\mu}_0,$$
$$\bar{C}_{44}^{-0} = 4\bar{\mu}_0^2 S_{44} - \bar{\mu}_0, \quad \bar{C}_{14}^{-0} = 4\bar{\mu}_0^2 S_{14}, \tag{B.10}$$

$$\bar{\theta} = \frac{3\bar{k}_0 + \bar{\mu}_0}{3\bar{k}_0 + 4\bar{\mu}_0}. \tag{B.11}$$

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