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Estimating elastic constants by averaging over simulated structures☆

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Abstract

In the context of atomistic simulations of solids, two situations often occur: that in which disordered structures (e.g. from “amorphous cell” simulations) are deemed to occur with essentially equal likelihood to form a “glass”, and that in which a particular orientational average over one crystal unit cell is desired, e.g. when a fiber modulus is deduced surmising that identical crystallites are oriented in the direction of the fiber axis with a specified direction of the unit cell frame while all orientations in the transverse directions are equally likely (“fiber symmetry”). The common averaging of elastic constants yields inappropriate results. We apply methods introduced by Hill and by Walpole more than three decades ago and show that with these methods, physically reasonable, self-consistent averages for elastic constants can be obtained as well as bounds considerably narrower than the well-known ones after Voigt and Reuss. © 2001 Published by Elsevier Science Ltd.

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1. The problem

The overall mechanical properties of materials comprising different domains cannot be estimated, in general, without detailed knowledge of the morphology of the material. For composites, this is usually done by either assuming some simplifying distribution of features (e.g. a random distribution of spheres in a matrix) and applying a theoretical solution, or numerically, starting from a configuration known in detail. Atomistic simulations are similar to calculations on composites: observed on a macroscopic level, most materials are homogeneous, but if observation focuses on ever smaller length scales, they become heterogeneous at some point. Even amorphous polymers are heterogeneous, if only on a scale of a few nanometers. This heterogeneity manifests itself in simulation when different realizations of e.g. an “amorphous cell” are employed to simulate properties: the simulated values differ from cell to cell, sometimes substantially, and a single cell usually is not perfectly isotropic in its characteristics. The question then is: what shall one do with sets of values obtained by simulation?[1]

We represent the isothermal elastic constants, statistical-mechanically defined as the elements of the fourth-rank tensor of second derivatives of Helmholtz energy A (per unit volume) with the tensor components of strain ε (or, employing the statistical–mechanical definition of strain, by the strain dependence of the material stress tensor $\boldsymbol{\sigma}$ [1])

$$C_{iklm} = \frac{1}{\langle V\rangle}\frac{\partial^2 A}{\partial\varepsilon_{ik}\,\partial\varepsilon_{lm}}\bigg|_{T,[\varepsilon_{ik}],[\varepsilon_{lm}]} \equiv \frac{\partial\sigma_{ik}}{\partial\varepsilon_{lm}}\bigg|_{T,[\varepsilon_{lm}]} \tag{1}$$

$\{i,j,k,l\}^4 \in \{1,2,3\}^4$

in the contracted matrix form [2,3], by

$$\mathbf{e} \equiv \begin{bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ 2\varepsilon_{23} \\ 2\varepsilon_{13} \\ 2\varepsilon_{12} \end{bmatrix} \qquad \mathbf{s} \equiv \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{13} \\ \sigma_{12} \end{bmatrix}$$

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[1] For properties that are determined by very local structural features, such as the cohesive energy or conformational features, a simple (or weighted) average over the different values obtained from different cells is certainly appropriate. For properties that involve interactions over large distances, where the macroscopic characteristic is determined by the interplay of many different volume elements, the answer is not that simple. The prime example of such properties are the elastic constants.

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$$\mathbf{C} \equiv \begin{bmatrix} C_{1111} & C_{1122} & C_{1133} & C_{1123} & C_{1113} & C_{1112} \\ C_{1122} & C_{2222} & C_{2233} & C_{2223} & C_{2213} & C_{2212} \\ C_{1133} & C_{2233} & C_{3333} & C_{3323} & C_{3313} & C_{3312} \\ C_{1123} & C_{2223} & C_{3323} & C_{2323} & C_{2313} & C_{2312} \\ C_{1113} & C_{2213} & C_{3313} & C_{2313} & C_{1313} & C_{1312} \\ C_{1112} & C_{2212} & C_{3312} & C_{2312} & C_{1312} & C_{1212} \end{bmatrix} \qquad (2)$$

where $\mathbf{e}$ is the "strain matrix," $\mathbf{s}$ the "stress matrix," and $\mathbf{C}$ the "stiffness matrix". The inverse $\mathbf{S} = \mathbf{C}^{-1}$ is the "compliance matrix" and $\mathbf{s} = \mathbf{Ce}$, $\mathbf{e} = \mathbf{Ss}$. The strain tensor ε_{ij} is symmetric by construction and the reduction to $\mathbf{e}$ does not involve a loss of information; the stress tensor σ_{ij} is only symmetric in mechanical equilibrium and the contracted matrix representation $\mathbf{s}$ only fully represents the stress tensor if mechanical equilibrium is established — this can happen in a static situation (e.g. for an energy-minimized single structure), or when the investigated material executes symmetric fluctuations around a mechanically equilibrated average configuration (e.g. when sufficiently many structures are considered that represent fluctuations). Due to the symmetry of ε_{ij} and σ_{ij} (in the mechanically equilibrated case), the tensor of elastic constants C_{iklm} is pair-wise symmetric in i, k and l, m and there are at most 21 independent tensor elements — typically these are identified with the 21 independent elements of the stiffness (or compliance) matrix. The elastic deformation energy is $1/2\mathbf{e}^{\mathrm{T}}\mathbf{s} = 1/2\mathbf{s}^{\mathrm{T}}\mathbf{e} = 1/2\mathbf{e}^{\mathrm{T}}\mathbf{Ce} = 1/2\mathbf{s}^{\mathrm{T}}\mathbf{Ss}$ (where the superscript "T" denotes the transpose, i.e. 1×6 matrices), and, since this energy must be positive, the stiffness matrix as well as the compliance matrix are positive definite.

The elements of $\mathbf{C}$ and $\mathbf{S}$ are addressed with their matrix subscripts, e.g. C_{25} (which is the same as the tensor component C_{2213}), and matrices from different simulations are distinguished with a single subscript, e.g. $\mathbf{C}_i$. The traditional moduli, i.e. the elastic moduli E_i, the shear moduli G_i, and Poisson's ratios ν_{ij} are defined as (the summation equation does not apply!)

$$E_i = \frac{1}{S_{ii}} \qquad G_i = \frac{1}{S_{kk}} \qquad \nu_{ij} = \frac{S_{ij}}{S_{jj}} \qquad (3)$$

$$\{i,j)^2 \in \{1,2,3\}^2 \;\; k = i+3$$

For the estimation of the composite elastic constants of a material composed of domains with different elastic properties, we follow Hill [4,5], Walpole [6,7], and Arridge [8] who treat elastic deformations of materials consisting of agglomerates of homogeneous solid domains firmly bonded together, i.e. "composites", in unbounded phases. Each domain has its own set of elastic constants and the volume of interest is "representative", i.e. sufficiently large that the heterogeneities of structure are averaged and the volume appears "macroscopically uniform". The approach chosen is one typical for "homogenization theories" [9,10]. The question to be answered is: "given an assembly of n $\mathbf{C}$s, $\{\mathbf{C}_i\}$, what is the appropriate average to represent the elastic constant matrix $\langle\mathbf{C}\rangle$?" Formally, we want to apply an overall strain, the "system strain" $\mathbf{e}_{\mathrm{SYS}}$ and ask for that stiffness matrix which produces the observed overall stress, the "system stress" $\mathbf{s}_{\mathrm{SYS}}$,

$$\mathbf{s}_{\mathrm{SYS}} = \langle\mathbf{C}\rangle\mathbf{e}_{\mathrm{SYS}} \qquad \text{or, alternatively,} \quad \mathbf{e}_{\mathrm{SYS}} = \langle\mathbf{S}\rangle\mathbf{s}_{\mathrm{SYS}} \qquad (4)$$

Note that the existence of such average matrices is not assured; for a system with a single ellipsoidal inclusion in an infinite continuum, Eshelby has found such a solution [11,12], and it has also been shown that they exist for multiple such inclusions in a periodic continuum [13], but for the general case this is not necessarily true. We limit ourselves to cases where only the frequency of occurrence (i.e. the volume fraction in the composite) of a particular structure is of relevance — neither shape nor size of a component shall be taken into account — and there are solutions to Eq. (4) in those situations.

In the context of atomistic simulations of solids, two situations are most common: (i) that in which a particular orientational average over one crystal unit cell is desired, e.g. when a fiber modulus is deduced surmising that identical crystallites are oriented in the direction of the fiber axis with a specified direction, fixed in the unit cell frame, while all orientations in the transverse direction are equally likely ("fiber symmetry"), or where a few crystal unit cells coexist, each subject to the same overall orientational disorder; and (ii) that in which disordered structures are deemed to occur with essentially equal likelihood, i.e. form a "glass". In these situations, the different domains are of unspecified shape but are firmly bonded together. Each structure to be counted in the averaging process is of equal weight and simple arithmetic means are calculated, i.e. $\langle a\rangle = \sum \phi_i a_i$, where ϕ_i is the volume fraction of structure i ($\sum \phi_i = 1$); in the common case (in simulations) that the volumes of all structures are identical, $\langle a\rangle = (1/n)\sum a_i$. It would be straightforward to modify the following schemes to include an averaging with specific weighting, e.g. with a Boltzmann weight so that $\langle a\rangle = \sum g_i\phi_i a_i$ with $g_i = \exp(-V_i/\mathrm{k}T)$, where V_i is the potential energy of the structure.

2. Voigt and Reuss bounds

The first treatments of the problem at hand by Voigt [14] and by Reuss [15] led to simple bounds that can readily be shown [8] to constitute strict upper and lower bounds, respectively (of course, the constituent materials must be elastic, i.e. have matrices of elastic constants that are symmetric and positive definite). Assuming that every domain in the composite is subjected to the same strain leads to the mean stiffness matrix as a simple average of the individual stiffness matrices, the Voigt bound:

$$\langle\mathbf{C}\rangle_{\mathrm{Voigt}} = \sum_i \phi_i\mathbf{C}_i$$

$$\text{or, if all volumes are equal, } \langle\mathbf{C}\rangle_{\mathrm{Voigt}} = \frac{1}{n}\sum_i \mathbf{C}_i. \qquad (5)$$

This is the extreme upper bound. The assumption that every domain in the composite feels the same stress gives the mean compliance matrix as a simple average of the individual compliances, the Reuss bound:

$$\langle \mathbf{S} \rangle_{\text{Reuss}} = \sum_i \phi_i \mathbf{S}_i \quad \text{or, if all volumes are equal,} \quad \langle \mathbf{S} \rangle_{\text{Reuss}} = \frac{1}{n}\sum_i \mathbf{S}_i. \tag{6}$$

$\langle \mathbf{C} \rangle_{\text{Reuss}} \equiv \langle \mathbf{S} \rangle_{\text{Reuss}}^{-1}$ is the extreme lower bound.

While Eqs. (5) and (6) are simple, they are also unnecessarily harsh. As pointed out by Hill [16] and Arridge [8], the forces between the domains in the Voigt average cannot be in equilibrium, whereas in the Reuss average the distorted domains cannot fit together. There are, fortunately, better possibilities. For special cases with known domain shapes and for some of the elastic moduli, for instance, the often used Hashin–Shtrikman bounds [17] apply. Less well-specified cases require different solutions. We discuss one possible avenue below.

3. Hill–Walpole averages

When the composite is deformed, each homogeneous solid domain can be considered, approximately, to be imbedded in a homogeneous material of the average properties of the mixture, the so-called "comparison material". For a single spherical inclusion in an infinite, homogeneous, strained elastic body, Eshelby [11] has found expressions relating the deformation of the inclusion with that of the overall system with the help of an "overall constraint" tensor (comprising elastic constants of the infinite matrix only) that describes the loading over the interface of the inclusion. Hill [4,5] and Walpole [6,7] applied this overall constraint tensor of an isotropic continuum with a spherical cavity to composites.

The Hill–Walpole approach requires the definition of a comparison material with constraint tensor corresponding to a stiffness matrix $\mathbf{C}^*$ or its inverse $\mathbf{S}^*$. The constraint tensor's form depends on the symmetry of the overall material and is written below for isotropic and cylindrically symmetric (fiber symmetry) domains. In either case, the mean stiffness matrix is obtained by

$$(\langle \mathbf{C} \rangle_{\text{HW}} + \mathbf{C}^*)^{-1} = \sum_i \phi_i (\mathbf{C}_i + \mathbf{C}^*)^{-1} \tag{7}$$

Note that for $\mathbf{C}^* = 0$, this gives the Reuss average. If all volumes are equal, this is conveniently written as

$$\langle \mathbf{C} \rangle_{\text{HW}} = \left(\frac{1}{n} \sum_i (\mathbf{C}^* + \mathbf{C}_i)^{-1} \right)^{-1} - \mathbf{C}^*. \tag{8}$$

For the compliance matrix, one obtains analogously

$$(\langle \mathbf{S} \rangle_{\text{HW}} + \mathbf{S}^*)^{-1} = \sum_i \phi_i (\mathbf{S}_i + \mathbf{S}^*)^{-1} \tag{9}$$

Here, for $\mathbf{S}^* = 0$, the Voigt average is obtained. If all volumes are equal, one can write

$$\langle \mathbf{S} \rangle_{\text{HW}} = \left(\frac{1}{n} \sum_i (\mathbf{S}^* + \mathbf{S}_i)^{-1} \right)^{-1} - \mathbf{S}^*. \tag{10}$$

Which of Eq. (7) or Eq. (10) is applied, depends on whether $\mathbf{C}^*$ or $\mathbf{S}^*$ is more convenient to use (they might be singular and, hence, not simply invertible). In any case, $\langle \mathbf{C} \rangle_{\text{HW}} = \langle \mathbf{S} \rangle_{\text{HW}}^{-1}$.

It is worthwhile to point out that the derivation of Eqs. (7) and (9) is based on the fact that the stiffness and compliance tensors of homogeneous elastic materials are symmetric and positive definite. The equations might not be applicable to situations where even one, or a few, of the $\mathbf{C}_i$ (or $\mathbf{S}_i$) are not symmetric or not positive definite. While there are simple (and justifiable) ways around the lack of symmetry in a matrix one might obtain from a particular simulation method (e.g. from molecular dynamics), such as replacing all off-diagonal elements by the mean of their symmetric siblings, it is less obvious what should be done with a matrix that is not positive definite, short of discarding it. We will address this question in Section 4 by considering some examples.

A self-consistent approach requires that the comparison material has the same properties as the average material, i.e. that the elastic constants, which define $\mathbf{C}^*$ are the same as those found from $\langle \mathbf{C} \rangle_{\text{HW}}$, and analogously for the compliances. In simulations, the stiffness and compliance matrices often contain values with rather large error and it might not be possible to satisfy these demands in detail. Some elastic invariants, determined by the symmetry of the comparison material, can be substituted for the full matrices, however, and Eqs. (7) and (9) can be solved iteratively to yield composite averages with elastic invariants in agreement with those of the reference materials. This approach yields "best" values for the elastic invariants. Below, we will term these values "Hill–Walpole averages".

3.1. Comparison material for an isotropic glass

An isotropic elastic material has a stiffness matrix with only two independent elastic constants. It is often written in the form

$$\mathbf{C} \equiv \begin{bmatrix} \lambda + 2\mu & \lambda & \lambda & 0 & 0 & 0 \\ \lambda & \lambda + 2\mu & \lambda & 0 & 0 & 0 \\ \lambda & \lambda & \lambda + 2\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & \mu & 0 & 0 \\ 0 & 0 & 0 & 0 & \mu & 0 \\ 0 & 0 & 0 & 0 & 0 & \mu \end{bmatrix} \tag{11}$$

where λ and μ are the Lamé constants. The traditional moduli B (bulk or compression modulus), G (shear modulus), E (Young's modulus), and ν (Poisson's ratio), expressed in Lamé constants, are

$$B = \lambda + \frac{2}{3}\mu \qquad G = \mu \qquad E = 2\mu(1 + \nu)$$
$$\nu = \frac{\lambda}{2(\lambda + \mu)} \tag{12}$$

The Lamé constants of a stiffness matrix from simulation can be obtained via a least-square procedure:

$$\mu = \frac{4a - 2b + 3c}{33} \qquad \lambda = \frac{2a + c - 15\mu}{6} \tag{13}$$

with

$$a = C_{11} + C_{22} + C_{33}$$
$$b = C_{12} + C_{13} + C_{21} + C_{23} + C_{31} + C_{32}$$
$$c = C_{44} + C_{55} + C_{66}$$

The overall constraint tensor of the isotropic comparison material [5] can be written in terms of the Lamé constants (of the comparison material):

$$C^*_{ijkl} = \frac{\mu}{2(3\lambda + 8\mu)}((2\lambda + 12\mu)\delta_{ij}\delta_{kl} + (9\lambda + 14\mu)(\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk})) \tag{14}$$

which is conveniently represented in Voigt notation as

$$\mathbf{C}^* = \frac{\mu}{2(3\lambda + 8\mu)}\begin{bmatrix} 20\lambda + 40\mu & 2\lambda + 12\mu & 2\lambda + 12\mu & 0 & 0 & 0 \\ 2\lambda + 12\mu & 20\lambda + 40\mu & 2\lambda + 12\mu & 0 & 0 & 0 \\ 2\lambda + 12\mu & 2\lambda + 12\mu & 20\lambda + 40\mu & 0 & 0 & 0 \\ 0 & 0 & 0 & 9\lambda + 14\mu & 0 & 0 \\ 0 & 0 & 0 & 0 & 9\lambda + 14\mu & 0 \\ 0 & 0 & 0 & 0 & 0 & 9\lambda + 14\mu \end{bmatrix} \tag{15}$$

and can be employed in Eqs. (7) and (8).

3.2. Comparison material for an aligned phase with fiber symmetry

An elastic material with fiber symmetry, i.e. one in which a C_∞ axis acts as fiber axis, has a stiffness matrix with five independent elastic constants [18]. For a system where the fiber axis is identified with the 3-axis, it can be written in the form [19][2]

$$\mathbf{C} \equiv \begin{bmatrix} K+M & K-M & L & 0 & 0 & 0 \\ K-M & K+M & L & 0 & 0 & 0 \\ L & L & N & 0 & 0 & 0 \\ 0 & 0 & 0 & P & 0 & 0 \\ 0 & 0 & 0 & 0 & P & 0 \\ 0 & 0 & 0 & 0 & 0 & M \end{bmatrix} \tag{16}$$

where K, L, M, N, and P are the fiber moduli [7], which are of course invariant to rotation around the 3-axis. The traditional extensional modulus (Young's modulus, E_3), the torsional modulus ($G_1 = G_2$), the extensional Poisson's ratio ($\nu_{13} = \nu_{23}$), and the transverse Poisson's ratio ($\nu_{12} = \nu_{21}$), expressed in fiber moduli, are

$$E_3 = N - L^2/K \qquad G_1 = G_2 = P \qquad \nu_{13} = \nu_{23} = L/2K$$
$$\nu_{12} = \nu_{21} = \frac{N(K - M) - L^2}{N(K + M) - L^2} \tag{17}$$

The fiber moduli of a stiffness matrix from simulation for any crystal class can be obtained, e.g. via:

$$K = \frac{C_{11} + C_{12} + C_{21} + C_{22}}{4}$$
$$L = \frac{C_{13} + C_{23} + C_{31} + C_{32}}{4}$$
$$M = \frac{C_{11} - C_{12} - C_{21} + C_{22} + C_{66}}{5} \qquad N = C_{33} \tag{18}$$
$$P = \frac{C_{44} + C_{55}}{2}$$

The overall constraint tensor of an aligned comparison material with fiber symmetry has been derived by Walpole[2]

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[2] Walpole [7] represents tensors in symbolic form. The stiffness tensor for materials with fiber symmetry is $\mathbf{C} = (2K, L, N, 2M, 2P)$ in this notation, which gives the fourth-rank tensor components as [19] $C_{1111} = K + M$, $C_{1122} = K - M$, $C_{1133} = L$, $C_{3333} = N$, $C_{2323} = C_{3131} = P$, and $C_{1212} = M$. The compliance constraint tensor $\mathbf{S}^*$ in symbolic notation is [7] $\mathbf{S}^* = (1/2M, 0, 0, (1/2M) + (1/2K), 1/2P)$, and hence, $S^*_{1111} = (1/2M) + (1/4K)$, $S^*_{1122} = -(1/4K)$, $S^*_{1133} = 0$, $S^*_{3333} = 0$, $S^*_{2323} = S^*_{3131} = 1/4P$, and $S^*_{1212} = (1/4M) + (1/4K)$, which is Eq. (19).

[19] for the compliances. This tensor is singular and the stiffness constraints cannot readily be obtained. We give here the overall compliance constraint matrix in the contracted notation (in terms of the comparison material's three relevant fiber moduli, K, M, and P):

$$\mathbf{S}^* = \frac{1}{4}\begin{bmatrix} \frac{2}{M}+\frac{1}{K} & -\frac{1}{K} & 0 & 0 & 0 & 0 \\ -\frac{1}{K} & \frac{2}{M}+\frac{1}{K} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{P} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{P} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{M}+\frac{1}{K} \end{bmatrix} \tag{19}$$

Application in Eq. (9) or (10) yields the desired results.

4. Hill–Walpole bounds

Eqs. (7) and (9) can be used to obtain bounds by observing that the comparison material for any of the domains cannot possibly have elastic invariants lying outside the range of the invariants of all domains in the composite (we use the term "elastic invariant" for measures of the tensor of elastic constants that are invariant to symmetry transformations consistent with the system symmetry — e.g. for the isotropic case, the two Lamé constants are invariant to rotation about any axis; in the case with fiber symmetry, the five fiber moduli are invariant to rotation about the fiber axis). The approach here is (i) to compute the elastic constants of all $\mathbf{C}_\mathrm{i}$, (ii) to select the upper and lower limits of the ranges spanned by the invariants, (iii) to calculate a different $\mathbf{C}^*$ for every combination of extreme invariants, and then (iv) to use Eq. (7) or Eq. (9) to compute a set of $\langle\mathbf{C}\rangle_{\mathrm{HW}}$ for every combination of extreme invariants; these averages span all possible values and their extremes provide new bounds, which we will term "Hill–Walpole bounds".

The situation most common in the simulation of mechanical properties of materials is that where for a homogeneous isotropic material, stiffness matrices are computed that show differences in the values of their elements. We chart a simple course for determining the Hill–Walpole bounds for these materials: two moduli, arbitrarily selected to be B and G, are calculated for every matrix $\mathbf{C}_\mathrm{i}$ using Eqs. (12) and (13), and the extremes in these two moduli are then taken to define four comparison materials through $\mathbf{C}^*$, Eq. (15): that with minimal B and minimal G, that with minimal B and maximal G, etc. Application of Eq. (7) with these four $\mathbf{C}^*$ then yields four different $\langle\mathbf{C}\rangle_{\mathrm{HW}}$ and from these in turn we obtain values for the traditional moduli. The extreme values of these are considered to be the Hill–Walpole bounds. The choice of moduli for this procedure is arbitrary and one could equally well choose E and ν instead of B and G, or another combination of two of the moduli; since the extremes in the combination of any two of the moduli correspond also to extremes in the others, the result will be identical. This fortunate circumstance might not hold for other symmetry classes where many moduli are required for the full specification of the matrix of elastic constants.

For the materials with fiber symmetry, stiffness matrices rotated about the fiber axis all have the same invariant fiber moduli K, L, M, N, and P — there is no basis to estimate bounds since there are no variations between the matrices. The elastic constants nevertheless require appropriate averaging.

5. Examples

5.1. Amorphous glassy polymers — aPS

As an illustration, atactic polystyrene at 300 K was taken (the values assumed [20] are representative for PS: $E = 3.4$ GPa, $G = 1.2$ GPa, $B = 5.0$ GPa, $\nu = 0.38$). The corresponding stiffness matrix is

$$\mathbf{C}_{\mathrm{PS}} = \begin{bmatrix} 6.6 & 4.2 & 4.2 & 0 & 0 & 0 \\ 4.2 & 6.6 & 4.2 & 0 & 0 & 0 \\ 4.2 & 4.2 & 6.6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1.2 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1.2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1.2 \end{bmatrix} \mathrm{GPa} \tag{20}$$

We want to test the procedures suggested in Section 3 concerning the stability of the self-consistent estimates of mean values and those from Section 4 with respect to narrowness of bounds obtained. Furthermore, we want to check these procedures regarding their sensitivity with respect to the two common deficiencies in simulated data: sometimes the matrices are asymmetric, sometimes not positive definite. To this end, test sets are required; they were derived from the stiffness matrix in Eq. (20). The volumes of all structures were identical and Eq. (8) was applied.

Sets of eleven stiffness matrices each (the test "data") were obtained from the above matrix in two ways: first, "random noise" from a uniform distribution with variable maximum amplitude was added to the individual elements of the stiffness matrix $\mathbf{C}$, in some cases preserving the symmetry of the matrix. Not all of these matrices were positive definite, as it might occur in stiffness matrices obtained from simulations. The second method used to

Table 1
Bounds and self-consistent means for sets of eleven structures derived from $\mathbf{C}_{\mathrm{PS}}$ for atactic polystyrene

Model system		G (GPa)	B (GPa)	E (GPa)	ν
"Parent" material		1.2	5.0	3.4	0.38
Random noise,[a] $\Delta = 1$ GPa (non-symmetric **C**s, one is non-positive definite)	Reuss/Voigt bounds	0.86/1.28	4.73/4.99	2.44/3.54	0.38/0.41
	Hill–Walpole average	1.12	4.88	3.13	0.39
	Hill–Walpole bounds	1.12/1.16	4.87/4.90	3.11/3.21	0.39/0.39
Random noise,[b] $\Delta = 1$ GPa (symmetric **C**s, five are non-positive definite)	Reuss/Voigt bounds	0.86/1.28	4.73/4.99	2.44/3.54	0.38/0.41
	Hill–Walpole average	1.12	4.88	3.13	0.39
	Hill–Walpole bounds	1.12/1.16	4.87/4.90	3.11/3.21	0.39/0.39
Random noise,[a] $\Delta = 2.5$ GPa (non-symmetric **C**s, seven are non-positive definite)	Reuss/Voigt bounds	0.76/1.33	5.01/5.09	2.17/3.66	0.38/0.43
	Hill–Walpole average		Did not converge		
	Hill–Walpole bounds	1.10/2.82	2.65/5.14	3.08/7.16	0.26/0.40
Evenly spaced B and G,[c] spanning $B = 0.6$–1.8 GPa and $G = 2.5$–7.5 GPa	Reuss/Voigt bounds	1.07/1.20	4.45/5.00	2.97/3.33	0.39/0.39
	Hill–Walpole average	1.14	4.60	3.17	0.39
	Hill–Walpole bounds	1.12/1.16	4.54/4.65	3.11/3.21	0.39/0.39

[a] The stiffness matrix of aPS and 10 matrices derived from it by adding "random noise" from a uniform distribution with maximum amplitude Δ to the individual elements. Negative matrix elements were replaced by their absolute values.

[b] As in previous footnote, but the matrices have been made symmetric ($C_{ij} = C_{ji}$).

[c] The matrices were computed from Eqs. (11) and (12), B and G assuming the values (2.5, 0.60), (3.0, 0.72), (3.5, 0.84), (4.0, 0.96), (4.5, 1.08), (5.0, 1.20), (5.5, 1.32), (6.0, 1.44), (6.5, 1.56), (7.0, 1.68), (7.5, 1.80), respectively.

obtain test sets consisted of computing matrices by Eqs. (11) and (12); values for B and G were selected uniformly spaced between 50 and 150% of the values given by Eq. (20) and stiffness matrices calculated from them (here, it does not matter whether the two invariants are changed in a parallel or an anti-parallel fashion). The second method provides test sets that are by construction symmetric and positive definite.

The variance of relevant parameters in these test sets is considerable. In the case where random noise was arbitrarily added to the elements of **C**, the values of, for instance, B varied between ca. 4.5 and 5.4 GPa when the maximum amplitude of the noise, Δ, was 1 GPa, and between 4.2 and 5.8 GPa when it was 2.5 GPa. In the case of the systematically changed sets, the values fell between 2.5 and 7.5 GPa.

Application of the procedures outlined above proceeded now as follows: the Voigt bound and the Reuss bound in the contracted representations were calculated by simply averaging all matrix elements over all matrices according to Eqs. (5) and (6), and the Lamé constants and the traditional moduli were obtained by Eqs. (12) and (13). For the Hill–Walpole bounds, B and G were calculated for every matrix, and the extremes in these two moduli were then taken to define four comparison materials through $\mathbf{C}^*$, Eq. (15): that with minimal B and minimal G, that with minimal B and maximal G, etc. Application of Eq. (8) with these four $\mathbf{C}^*$ then yielded four different $\langle \mathbf{C} \rangle_{\mathrm{HW}}$ and from these in turn we obtained values for the traditional moduli. The extreme values of these are listed in Table 1 as Hill–Walpole bounds. The Hill–Walpole averages, i.e. the self-consistent mean values of the elastic constants, were determined by starting with one particular comparison material, computing $\langle \mathbf{C} \rangle_{\mathrm{HW}}$ via Eq. (8), extracting the traditional moduli, using those to define a new comparison material, and repeating this process until convergence had been reached. Here we considered the process as having converged when none of the elements of $\langle \mathbf{C} \rangle_{\mathrm{HW}}$ between two iterations changed by more than 0.1% of the maximum matrix element. It was found that when the method converged, it did so in no more than two iterations; also, runs started with different comparison materials yielded the same result. In one case, where more than two-thirds of all matrices in the data set were not positive definite, the method did not converge at all — it is our contention that no solution exists for this very inappropriate data set.

Inspecting the values in Table 1, the following is evident: (i) modest asymmetry in the data matrices does not seem to

Table 2
Hill–Walpole averages for elastic constants from rotational averaging of $\mathbf{C}_{\mathrm{PPTA}}$ to fiber symmetry

Quantity	Reuss and Voigt bounds	Hill–Walpole average
Extensional modulus, E_3	273/335	309
Transverse modulus, $E_1 = E_2$	16.7/20.3	19.7
Torsional moduli, $G_1 = G_2$	6.7/13.7	12.0
Extensional Poisson's ratio, $\nu_{13} = \nu_{23}$	0.46/0.53	0.51
Transverse Poisson's ratio, $\nu_{12} = \nu_{21}$	0.62/0.66	0.62

have a perceptible effect on the results; (ii) once the data is sufficiently "corrupted", as in the case of the randomly perturbed data with noise amplitudes up to 2.5 GPa (the peak-to-peak noise was 75% of the largest element of the "parent" matrix), a self-consistent Hill–Walpole mean cannot be found. An indication of the insufficiency of the data is the fact that the Hill–Walpole bounds span a larger range than the Voigt/Reuss bounds (remember that the Voigt/Reuss bounds are strict upper and lower bounds only for sets of symmetric and positive definite matrices of elastic constants); (iii) for data of reasonable quality, the Hill–Walpole approach provides an efficient path to a physically reasonable average of all elastic constants and to bounds considerably narrower than those available before.

5.2. Polymer fiber — PPTA

A crystalline polymer from the literature was selected as test case: a simulated crystal cell [21] of poly(*p*-phenylene terephthalate), PPTA, similar in atomistic structure to this polymer's modification I. The stiffness matrix is [21]

$$\mathbf{C}_{\mathrm{PPTA}} = \begin{bmatrix} 40 & 23 & 13 & 0.1 & 1.2 & 2.4 \\ 23 & 31 & 41 & 1.5 & 3.2 & 1.9 \\ 13 & 41 & 360 & 0.3 & 5.0 & 11 \\ 0.1 & 1.5 & 0.3 & 5.5 & 3.7 & 2.7 \\ 1.2 & 3.2 & 5.0 & 3.7 & 22 & 3.2 \\ 2.4 & 1.9 & 11 & 2.7 & 3.2 & 1.2 \end{bmatrix} \mathrm{GPa} \qquad (21)$$

The fibers of PPTA are assumed to consist only of crystallites, which are all oriented with their 3-axis parallel to the fiber axis, their transversal orientation being random. For the processes of rotationally averaging this crystal structure to fiber symmetry, a number of derivative stiffness matrices are required that are uniformly distributed in orientation around the 3-axis. For the Voigt and Reuss bounds, this can readily be done analytically [21], but not for the Hill–Walpole method. We select four structures, each rotated by 90° around the 3-axis with respect to the preceding one,[3] in the averaging procedures.

Application of the approach outlined above proceeded now as follows: the Voigt bound and the Reuss bound in the contracted representation were calculated by simply averaging the matrix elements of the four matrices according to Eqs. (5) and (6) and the traditional moduli were obtained by Eqs. (17) and (18). The results are listed in Table 2.

The Hill–Walpole averages, i.e. the self-consistent mean values of the elastic constants, were determined by starting with one particular comparison material, computing $\langle \mathbf{S} \rangle_{\mathrm{HW}}$ via Eq. (10), extracting the traditional moduli, using those to define a new comparison material, and repeating this process until convergence had been reached. Here we considered the process as having converged when none of the elements of $\langle \mathbf{S} \rangle_{\mathrm{HW}}$ between two iterations changed by more than 0.1% of the maximum matrix element. The method converged in two iterations. The self-consistent average stiffness matrix is

$$\mathrm{PPTA} : \langle \mathbf{C} \rangle_{\mathrm{HW}}$$

$$= \begin{bmatrix} 35 & 23 & 29 & 0 & 0 & 0.2 \\ 23 & 35 & 29 & 0 & 0 & -0.2 \\ 29 & 29 & 338 & 0 & 0 & 0 \\ 0 & 0 & 0 & 12 & 0 & 0 \\ 0 & 0 & 0 & 0 & 12 & 0 \\ 0.2 & -0.2 & 0 & 0 & 0 & 7.1 \end{bmatrix} \mathrm{GPa} \quad (22)$$

The results for the moduli are reported in Table 2. These values clearly show that the Hill–Walpole approach provides an efficient path to a physically reasonable average of the elastic constants.

6. Conclusions

Two situations are very common in atomistic modeling: that in which a disordered material is represented by a number of independent structures, each with its own stiffness and compliance matrix, and where the mean stiffness and compliance of the macroscopic material, hypothetically

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[3] Rotated by 90° around the 3-axis, the stiffness matrix expressed in the original tensor element is:

$$\mathbf{C}_{\text{rot by 90° around 3-axis}}$$

$$= \begin{bmatrix} C_{2222} & C_{1122} & C_{2233} & C_{2213} & -C_{2223} & -C_{2212} \\ C_{1122} & C_{1111} & C_{1133} & C_{1113} & -C_{1123} & -C_{1112} \\ C_{2233} & C_{1133} & C_{3333} & C_{3313} & -C_{3323} & -C_{3312} \\ C_{2213} & C_{1113} & C_{3313} & C_{1313} & -C_{2313} & -C_{1312} \\ -C_{2223} & -C_{1123} & -C_{3323} & -C_{2313} & C_{2323} & C_{2312} \\ -C_{2212} & -C_{1112} & -C_{3312} & -C_{1312} & C_{2312} & C_{1212} \end{bmatrix}$$

consisting of many such structures, are requested, and that in which a particular orientational average of the stiffness or compliance matrix of one crystal unit cell is desired, e.g. when a fiber modulus is deduced assuming fiber symmetry. The common procedure of simply averaging elastic matrices in these situations is clearly inappropriate [8,16]. Instead, the methods introduced by Hill [4,5] and by Walpole [6,7] more than three decades ago for the evaluation of the overall elastic behavior of composites have here been applied, with success.

The contracted notation was found to be convenient for this problem and application of the Hill and Walpole methods to two simple model data sets shows that with these techniques, physically reasonable, self-consistent averages for elastic constants can be readily computed and that bounds considerably narrower than the well-known ones after Voigt and Reuss can be obtained. Short programs to effect the calculations described here can be obtained from the authors.

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