Homogenization of the elastic properties of pyrolytic carbon based on an image processing technique

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In this work, the linear elastic material properties of differently textured variants of pyrolytic carbon are homogenized from the submicro- to the micro-scale. In high resolution transmission electron microscope (HRTEM) lattice fringe images, the microstructure of pyrolytic carbon manifests itself in terms of projections of graphene layers. According to their orientation distribution, different textures of pyrolytic carbon have been classified. Assuming a von Mises-Fisher distribution for the spatial orientation of single graphene layers, the orientation distribution function of the projected layers in the image plane is analytically found to be a modified Struve function. For each pyrolytic carbon texture, Maximum-likelihood estimates for the mean orientation and the concentration parameter of the von Mises-Fisher distribution are obtained numerically. Hereby, Fourier transformation and appropriate filters are used to determine the probabilities for discrete orientations of the graphene layers directly from HRTEM images. First- and second-order bounds of the linear elastic properties of pyrolytic carbon of the different textures are computed. Elastic constants of graphite and pyrolytic graphite have been used for modeling the elastic behavior of the graphene layers within a continuum mechanical setting. Due to the high anisotropy of all analyzed textures of pyrolytic carbon, the differences even between the second-order bounds are quite large.

1 Introduction

Pyrolytic carbon (PyC) is a graphite-like material and is used as micro constituent of carbon/carbon (C/C) or carbon/silicon (C/Si) composites. Such composites combine light weight, exceptional strength, and stiffness with excellent refractory properties. Therefore, they can be used under severe thermal loadings, such as atmospheric re-entry, solid rocket motor exhaust, and disk brakes of high performance aircraft, high speed trains, and racing cars [10,14]. One method of the fabrication of C/C composites is the process of chemical vapor infiltration (CVI). In CVI a felt or oriented carbon fiber preform is heated to elevated temperatures (900°C–2200°C) and hydrocarbon gases such as methane, propane acetylene, etc. flow through the furnace. These gases decompose into heterocyclic carbon ring compounds [18,31] and deposit on the surface to form graphite-like structures with varying texture degrees. This form of carbon is termed PyC and exhibits transverse microstructural isotropy in the deposition plane [27].

The microstructure of PyC can be described by an ensemble of graphene planes and manifests itself in terms of projections of the graphene planes in high resolution transmission electron microscope (HRTEM) lattice fringe images. Depending on the width of the orientation distribution of the projected graphene layers Reznik and Hütttinger [28] proposed a classification scheme for the terminology of the PyC microstructure: low textured PyC (LT) (with a broad distribution), medium textured PyC (MT) and high textured PyC (HT) (with more and more narrow distributions) (see Fig. 1). Reznik et al. [27] correlated PyC texture obtained by polarized light microscopy with information from HRTEM images and selected area diffraction patterns (SAED). Combining different analysis methods like TEM, X-ray diffraction, and Raman spectroscopy, the influence of parameters of the manufacturing process on the microstructure of PyC has been studied by López-Honorato et al. [17]. Leyssale et al. [16] proposed a promising approach for atomistic reconstruction of pyrolytic carbons using statistical analysis of HRTEM images and synthesized 3D HRTEM-like images. Three typical HRTEM images of LT, MT, and HT are shown in Fig. 2 (Source: Dr. Reznik, KIT) and these images are analyzed in this paper later on. All three images possess the resolution of 1000 × 1000 pixels and scale of 0.05 × 0.05 nm²/pixel.

Several authors have studied the elastic properties of carbon-based materials. Gebert et al. [13] measured the components of the stiffness tensor of highly oriented PyC under assumption of the transversal isotropy by using ultrasound phase
spectroscopy on macroscopic samples. The elastic constants of single-crystal graphite have been determined by Bosak and Krisch [6] using inelastic x-ray scattering with dimensions of the x-ray beam being $250 \times 60 \, \mu m^2$. Blakslee et al. [7] have determined the elastic constants of pyrolytic graphite on macro-scale using ultrasonic tests. Gross et al. [11] have used standard strain gage methods to measure the in-plane and out-of-plane elastic modulus and Poisson’s ratio in tension and compression asymmetrically on macro level. Born’s long wave method has been applied by Michel and Verberck [21] to identify the elastic constants of graphite.

Relying on a continuum hypothesis, Böhlke et al. [5] have assumed a von Mises-Fisher distribution for the orientation of the graphene layers and have tried to link the concentration parameter of this distribution to the above mentioned terminology of PyC (HT, MT, and LT). It turned out that there is no easy relation between values of the concentration parameter and the PyC textures. Due to lack of experimentally determined material properties on nano-scale, a transversely isotropic mechanical behavior on the nano-scale has been assumed in the homogenization of the elastic properties of PyC from nano-scale to micro-scale [5].

Image processing techniques have been applied to extract quantitative structural information from HRTEM images of carbon blacks [32]. Palotás et al. [25] have used a fast Fourier transformation approach to quantify the structure of carbon blacks based on direct electron microscopic observations. The main objective of the present work is to gather statistical information directly based on HRTEM images by using image processing techniques for homogenization of elastic properties.

The outline of this work is as follows. First, Fourier-based analysis is used to determine the orientation distribution function of the projections of the layer planes in the image plane. This information is used to determine the plane orientation distribution function (PODF) by means of the von Mises-Fisher distribution. Following that, the estimates of the concentration parameter are discussed. Based on the assumption of transversely isotropic material behavior of the minimal homogeneous units, not only first-order, but also second-order bounds for the elastic properties of the different microstructures of PyC on micro-scale are presented. All results are obtained for the images in Fig. 2 and are discussed at the end.

**Notation.** A direct tensor notation is preferred throughout the text. If tensor components are used, then the Einstein summation convention is applied. Vectors and 2nd-order tensors are denoted by lowercase and uppercase bold letters, e.g., $\mathbf{a}$ and $\mathbf{A}$, respectively. A linear mapping of 2nd-order tensors by a 4th-order tensor is written as $\mathbf{A} = \mathcal{C}[\mathbf{B}]$. The scalar product
and the dyadic product are denoted, e.g., by $a \cdot b$ and $a \otimes b$, respectively. The composition of two 2nd-order or two 4th-order tensors is formulated by $AB$ and $\Lambda B$. $(A \otimes B)[C] = ACB \forall A, B, C$ and $(a \otimes b) \cdot (C[(a \otimes b)]) = (a \otimes a) \cdot (C[b \otimes b]) \forall a, b, C$ are defined. Completely symmetric and traceless tensors are designated by a prime, e.g., $A'$. The brackets $(\cdot)$, e.g., $\langle \cdot \rangle$, indicate ensemble averaging which for ergodic media can be identified with volume averages in the infinite volume limit. The symbol $\ast$ denotes the Rayleigh product, which for tensors $T = T_{ij...l} e_i \otimes e_j \otimes \ldots \otimes e_l$ of arbitrary rank is defined by $Q \ast T = T_{ij...l}(Qe_i) \otimes (Qe_j) \otimes \ldots \otimes (Qe_l)$. The product $Q \ast T$ can be interpreted as the rotation of the tensor $T$ by the orthogonal tensor $Q$. The tensor $I$ is the identity on vectors. The identity on symmetric 2nd-order tensors is denoted by $I^\circ$.

2 Laplacian of Gaussian filter and Fourier analysis

In image processing, the minimal unit within an image is called 'pixel' taking grey values as intensity information. It has the range from 0 to 255 for an 8-bit grey scale. By observing the HRTEM images of PyC in Fig. 2, pixels possess a consistent size for different types of microstructures, HT, MT, and LT (1 pixel = 0.05 × 0.05 nm²). Since the physical minimal layer spacing $d_{002}$ of PyC has been determined by Guellali et al. [12] to be 0.34 nm, one single layer plane is spatially resolved by several pixels. An image is a 2D-set of pixels which is considered as a 2D-grid. In the following, the positions in the horizontal direction and the vertical direction are denoted by variable $x_1$ and $x_2$, respectively.

![Image 1](https://www.zamm-journal.org)  

![Image 2](https://www.zamm-journal.org)  

Fig. 3 (a) An example image 100 × 100 pixels with pixel swapping frequency of five from black to white; (b) magnitude part of FT result for the example image in (a).

Fourier Transformation (FT) is an image processing tool which is used to decompose an image into a magnitude and a phase part. The FT detects the changing of grey values, which is called 'edge' in image processing. An example image is given in Fig. 3a. In the $x_1$ direction, the edges (swapping between the black and white pixels) are located every 5 pixels. In the present work, the relevant FT images are the magnitude part, which is defined by the absolute value of the FT. In the magnitude part of the FT, illustrated in Fig. 3b, the middle point $O$ denotes the null frequency and the other two points $f_1, f_2$ indicate the swapping frequency of the transitions from black to white pixels (positive frequency) and vice versa (negative frequency), respectively. Therefore, the points $f_1$ and $f_2$ are symmetric with respect to the middle point $O$. The distances of $O f_1$ and $O f_2$ correspond to 5 pixels. The direction of $f_1 f_2$ represents the normal direction of the edge of the striped lines in Fig. 3a. In the $x_2$ direction, the grey values do not change. Thus, there is only the null frequency in the $f_{x_2}$ direction of the frequency domain.

As shown in Fig. 4, the parallel layer planes are projected on the image plane as striped lines in an HRTEM image. The edges describe the contour shape of each layer plane on the image. To each pixel on the contour shape a normal vector can be assigned, which is perpendicular to the corresponding edge in the image plane. The distribution of the orientation of the graphene layers can be determined by the distribution of the normal vectors on edges using the Fourier-based analysis. By analogy with the $x_2$ direction in Fig. 3a, the pixels without the transition from black to white grey values are interpreted by a null frequency in the Fourier-based analysis. Hence, they will not influence the estimate of the orientation distribution of the layer planes on the image plane.
The magnitude parts of FT results for the HRTEM images HT, MT, and LT (see Fig. 2) are shown in Fig. 5. For raising the contrast of the image, the logarithm is applied on the each FT result. Since we aim to obtain the orientation distribution using the FT, the following image techniques are applied for the HRTEM images here.

A Laplacian filter is applied on an image smoothed by using a Gaussian filter. This two-step process is called Laplacian of Gaussian (LoG) operation and is defined by

$$\text{LoG}(x_1, x_2) = \frac{1}{\pi \sigma^4} \left(1 - \frac{x_1^2 + x_2^2}{2\sigma^2}\right) \exp \left(-\frac{x_1^2 + x_2^2}{2\sigma^2}\right).$$  

(1)

For minimizing the information loss, the window size of the LoG filter is chosen to be $5 \times 5$ pixels and $\sigma = 0.5$ in this work. The LoG operator takes the second derivative of the image. Where the image is basically uniform, the LoG result is zero. Wherever a change of grey values occurs, the LoG will give a positive response on the darker side and a negative response on the lighter side. After utilization of the LoG, the results of FT are improved in the sense of the contrast of the image (see Fig. 6).

In order to obtain an orientation distribution from the FT result, an integration in the frequency domain depending on the orientation is used. As shown in Fig. 7, the vertical red straight line is fixed and a dashed line is rotated around the central point counter-clockwisely. The angle $\alpha$ between the rotated dashed line and the vertical red straight line corresponds to the normal direction of the edges (e.g., see Fig. 3). For each angle $\alpha$ (from 1 to 180 degree), the amplitude values on the rotated line are integrated in frequency domain to yield the frequency of the layer planes. Based on the integrated frequencies depending on the angle $\alpha$ the probability of orientations under the angle $\alpha$ is obtained by normalization. The discretized probabilities of the orientation of the graphene layers in the HRTEM images of HT, MT, and LT (see Fig. 2) are shown in Fig. 8a–c, respectively.
Fig. 6 The FT results by preprocessing a LoG filter on the images of Fig. 2: (a) HT; (b) MT; (c) LT of PyC.

Fig. 7 (online colour at: www.zamm-journal.org) Line integration of FT result for Fig. 6a.

3 Pixel-based plane orientation distribution function

3.1 Motivation

The basic assumption within this work is that the microstructure of PyC can be described by a three-dimensional ensemble of graphene planes. For each plane, the orientation can be defined to be perpendicular to the tangent directions of the layer plane on an arbitrary point of the planar surface. Thus, every orientation can be described by a unit normal vector $c$. If a single fiber with a surrounding PyC layer is considered, the following coordinate system is introduced: the coordinate system is defined to have the $e_3$-axis parallel to the fiber-axis. In the HRTEM images presented in this paper, the image plane lies always in the $e_1 - e_2$ plane, i.e., perpendicular to the fiber-axis. Since the infiltration process induces a growth perpendicular to the fiber surface, the mean plane orientation lies approximately in the $e_1 - e_2$ plane. In the subsequent considerations each unit normal $c$ axis of an arbitrary plane is described in spherical coordinates with respect to the aforementioned coordinate system (see Fig. 9). As a result the $c$-axis is defined by the azimuthal angle $\varphi$ and the polar angle $\vartheta$

$$c(\varphi, \vartheta) = \cos(\varphi) \sin(\vartheta) e_1 + \sin(\varphi) \sin(\vartheta) e_2 + \cos(\vartheta) e_3.$$  \hspace{1cm} (2)

As shown in Fig. 10, each of the normal vectors $c$ can be projected into the plane $P$ and normalized giving the unit vector $c'$. The angles between the $c'$ and $c$ with the axis $e_1$ are denoted by $\alpha$ and $\gamma$, respectively.

This implies

$$c'(\alpha) = \cos(\alpha) e_1 + \sin(\alpha) e_2, \quad \alpha \in [0; \pi], \hspace{1cm} (3)$$

and

$$\bar{c}(\gamma) = \cos(\gamma) e_1 + \sin(\gamma) e_2, \quad \gamma \in [0; \pi]. \hspace{1cm} (4)$$
Fig. 8  (online colour at: www.zamm-journal.org) The discretized probabilities of the orientation of the graphene layers in the HRTEM images for HT, MT, and LT of PyC.

Fig. 9  Cross section plane $P$ of the fiber: the plane $P$ is described by the axes $e_1$ and $e_2$, the axis $e_3 = e_1 \times e_2$ is perpendicular to $P$. The $c$-axis, which is represented in spherical coordinates, has the projection $c'$ on the plane $P$.

3.2 Plane orientation distribution function

Every graphene plane can be locally described by a unit normal vector $c$, or equivalently by a proper orthogonal tensor $Q \in SO(3)$

$$c = Qc_0,$$

(5)

where $c_0$ is an arbitrary but constant reference unit normal vector identical for all layer planes. It should be noted that for given $c$ and fixed $c_0$, the tensor $Q$ is not unique since arbitrary rotations around $c_0$ or $c$ keep Eq. (5) invariant. Hence, $Q$ can be specified by two independent parameters instead of three parameters for the general orthogonal second-order tensor. This will be taken into account by the specific structure of the distribution function introduced later on. The plane orientation distribution function (PODF) $f_c(c)$ specifies the volume fraction $dv/v$ of the layer planes with a unit normal
Fig. 10 (online colour at: www.zamm-journal.org) The plane $P'$ is imaging plane of $P$ in Fig. 9. On the plane $P'$ the orientation $\alpha$, the angle $\gamma$ and the mean vector $\bar{c}$-axis are defined, where $\varphi = \alpha$.

vector $c$, i.e.,
\[
\frac{dv}{v}(c) = f_c(c) \, dc,
\]
where $dc$ is the surface element of the unit sphere $S^2$ in the three-dimensional Euclidean space. The PODF can be described equivalently by a distribution function $f(Q)$ specifying the volume fraction $dv/v$ with the orientation $Q$ [5], i.e.,
\[
\frac{dv}{v}(Q) = f(Q) \, dQ.
\]
Here, $dQ$ is the volume element in $SO(3)$ which ensures an invariant integration over $SO(3)$. The functions $f$ and $f_c$ are related by
\[
f(Q) = f_c(Qc_0).
\]

The function $f(Q)$ is non-negative and normalized $\int_{SO(3)} f(Q) \, dQ = 1$. The orientation distribution function $f(Q)$ reflects both the material symmetry of the planes forming the aggregate and the symmetry of the microstructure. The material symmetry of the single layer plane implies the following symmetry relation: $f(Q) = f(QH_D) \forall H_D \in SD \subseteq SO(3)$, where $SD$ denotes the material symmetry group. The symmetry of the microstructure implies $f(Q) = f(H_M^T Q) \forall H_M \in SM \subseteq SO(3)$, where $SM$ denotes the symmetry group of the microstructure. An orientation average $\bar{\psi}$ of a quantity $\psi(Q)$ defined on $SO(3)$ is generally given by
\[
\bar{\psi} = \int_{SO(3)} f(Q) \psi(Q) \, dQ.
\]

The equation $\bar{\psi} = \sum_{\alpha=1}^{N} c_{\alpha} \psi(Q_{\alpha})$ holds if the PODF is approximated by a set of $N$ Dirac distributions with corresponding weights $c_{\alpha}$. The weights satisfy the normalization condition: $\sum_{\alpha=1}^{N} c_{\alpha} = 1$, where $N$ denotes the number of the layer planes.

### 3.3 Von Mises-Fisher distribution

In this work, the PODF is modeled by the $c$-axes based on a one parameter axial orientation distribution function. The orientations of the graphene layers are described as random variables that are stochastically independent and identically distributed. Based on the central limit theorem, the sum of finitely many independent random variables tends to be distributed according to the Gaussian distribution in the Euclidean space. In directional statistics, the von Mises-Fisher distribution is an analogue to the Gaussian distribution on the unit spheres $S^2$ in $\mathbb{R}^3$ [9]. Taking into account the mean normal vector $\bar{c}$-axis, the von Mises-Fisher distribution (see e.g., [5, 20]) describes the concentration of distributed $c$-axes of planes on the orientation sphere. Thus, the probability density of the orientation of the unit normal vectors $c$ is generally given by
\[
f_c(c) = \frac{\kappa}{\sinh(\kappa)} \exp(\kappa \bar{c} \cdot c),
\]
where $\kappa$ is the concentration parameter of the von Mises-Fisher distribution. The vector $\bar{c}$ is the mean direction or expectation value of the $c$-vectors of the planes. The mean direction $\bar{c}$ is obtained by an orientation average of all layer planes.

The non-even function $f_c$ according to Eq. (10) is symmetrized
\[
f_c(c) = \frac{1}{2} \frac{\kappa}{\sinh(\kappa)} (\exp(\kappa \bar{c} \cdot c) + \exp(-\kappa \bar{c} \cdot c))
\]
in order to ensure \( f_c(e) = f_c(-e) \). Considering Eq. (5), one can obtain the orientation distribution function \( f(Q) \)

\[
f(Q) = \frac{1}{2} \frac{\kappa}{\sinh(\kappa)} (\exp(\kappa e \cdot (Qc_0)) + \exp(-\kappa e \cdot (Qc_0))).
\]

(12)

Using the von Mises-Fisher probability density (11) and Eqs. (2) and (4) the following representation for \( f_c(e) \) is obtained

\[
f_c(\varphi, \theta, \gamma) = \frac{1}{2} \frac{\kappa}{\sinh(\kappa)} \cosh(\kappa \sin(\theta) \sin(\varphi - \gamma)).
\]

(13)

For any unit normal vector of the layer planes, one geometrically obtains \( \varphi = \alpha \) (see Fig. 10) and can then define the probability density \( \tilde{f}_\kappa(\alpha, \gamma) \) for \( \alpha \) depending on the angle \( \gamma \) of the \( \bar{c} \) axis and on the concentration parameter

\[
\tilde{f}_\kappa(\alpha, \gamma) = \frac{1}{2} \frac{\kappa}{\sinh(\kappa)} L_{-1}(\kappa \cos(\gamma - \alpha)),
\]

(15)

where \( L_{-1}(\cdot) \) is the modified Struve function [1]. Its definition as power series is

\[
L_v(z) = \left(\frac{1}{2} z\right)^{v+1} \sum_{k=0}^{\infty} \frac{\left(\frac{1}{2} z\right)^{2k}}{\Gamma(k + \frac{3}{2}) \Gamma(k + v + \frac{3}{2})},
\]

(16)

where \( \Gamma(z) \) is the Gamma function. For \( \kappa \to 0 \) the result can be yielded from Eq. (15)

\[
\lim_{\kappa \to 0} \tilde{f}_\kappa(\alpha, \gamma) = \frac{1}{2\pi}.
\]

(17)

Note that for a given HRTEM image, the angle \( \gamma \) is fixed. Hence, \( \tilde{f}_\kappa \) is a function of \( \alpha \) and \( \kappa \). For the special case, \( \bar{c} = e_2 \) (i.e. \( \gamma = \pi/2 \)), the densities \( \tilde{f}_\kappa \) are plotted in Fig. 11 for different concentration parameters \( \kappa \). In the next section the estimation of the parameters \( \kappa \) and \( \gamma \) is discussed assuming that the distribution of the angles \( \alpha \) for the layer planes in an HRTEM image can be estimated by means of the FT (see Fig. 8).

Fig. 11 (online colour at: www.zamm-journal.org) Probability density function of the angle \( \alpha \) for \( \gamma = \pi/2 \) and different values of the concentration parameter \( \kappa \).

3.4 Estimation of distribution parameters

The distribution function Eq. (14) for the orientation of the graphene planes contains \( \gamma \), the mean orientation angle of the graphene planes, and \( \kappa \), the concentration parameter of the von Mises-Fisher distribution. Having obtained the distribution
of the orientations of the graphene planes by image processing for regions with definite texture HT, MT, and LT (see Fig. 2), the parameters $\gamma$ and $\kappa$ are determined separately for the three textures by the Maximum-Likelihood-method (e.g., [2]). Hereby, the log-likelihood function $\Psi_\alpha(\kappa, \gamma)$ is defined as follows:

$$
\Psi_\alpha(\kappa, \gamma) = \frac{N_s}{\sum_{i=1}^{N_s} \ln \left( \tilde{f}_\alpha(\alpha_i, \gamma) \right)},
$$

(18)

where $N_s$ represents the number of realizations of the orientation angles $\alpha_i$ of the graphene planes according to the probability distribution in Fig. 8. The plots of the log-likelihood functions for HT, MT, and LT PyC are represented in Fig. 12a-c, respectively. The figures show that an unique global maximum of the log-likelihood functions can be found for each of the three cases. This global maximum defines the best concentration parameter $\kappa$ and the best angle $\gamma$ for each texture. The estimated parameters are given in Table 1. Their dependence on the number of realizations $N_s$ for the log-likelihood-function has numerically been verified to be negligible, and $N_s = 10000$ realizations have been used.

![Fig. 12](online colour at: www.zamm-journal.org) 2D plots of log-likelihood functions for HT (a), MT (b), and LT (c).

**Table 1** Maximum-likelihood based estimates of distribution parameters for HT, MT, and LT in Fig. 2.

<table>
<thead>
<tr>
<th></th>
<th>$\kappa [-]$</th>
<th>$\gamma [^\circ]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HT</td>
<td>3.5</td>
<td>153</td>
</tr>
<tr>
<td>MT</td>
<td>1.9</td>
<td>141</td>
</tr>
<tr>
<td>LT</td>
<td>1.6</td>
<td>142</td>
</tr>
</tbody>
</table>

Having obtained the parameter $\kappa$ (see Table 1), it is possible to check the assumption of the von Mises-Fisher distribution for the concrete data of the HRTEM images. In Fig. 13, additionally to the probabilities of different orientations of the graphene planes from Fig. 8, now the von Mises-Fisher distribution has been included. For MT and LT this assumption fits very well and for HT the deviations are small. Thus the assumption of a von Mises-Fisher distribution for the orientation of the graphene planes is justified.
Fig. 13 (online colour at: www.zamm-journal.org) The von Mises-Fisher distribution with the estimated $\kappa$ and $\gamma$ for HT (a), MT (b), and LT (c).

Furthermore, pole figures (central projection) based on 10000 realizations and corresponding to von Mises-Fisher distributions with the estimated $\kappa$ values obtained for HT, MT, and LT PyC are shown in Fig. 14a–c.

Fig. 14 (online colour at: www.zamm-journal.org) Pole figures of (a) HT, (b) MT, and (c) LT PyC.

### 4 Homogenization of the elastic properties

#### 4.1 Elastic properties

Since only elastic deformations are considered, the stress-strain relationship is given by Hooke’s law $\sigma = C[\varepsilon]$. The Cauchy stress and the infinitesimal strain tensor are denoted by $\sigma$ and $\varepsilon$, respectively. The stiffness tensor $C$ is assumed to have the major and minor symmetries. The inverse stress-strain relationship is given by $\varepsilon = S[\sigma]$ with the compliance tensor $S$.

The elastic behavior is assumed to be elastically isomorphic such that there exists the following representation for the position dependent stiffness tensor $\mathcal{C}(x) = \mathcal{C}(Q(x)) = Q(x) \ast \mathcal{\hat{C}}$, with a constant and homogeneous reference stiffness $\mathcal{\hat{C}}$ and the local orientation of the graphene planes given by $Q$. 
It is reasonable to assume a transversely isotropic elastic behavior such that five independent constants and the orientation of the graphene layers specifies the elasticity tensor $C$, completely. The transversely isotropic reference stiffness $\tilde{C}$ has the representation

$$\tilde{C} = \begin{bmatrix}
C_{1111} & C_{1122} & C_{1133} & 0 & 0 & 0 \\
C_{1111} & C_{1133} & 0 & 0 & 0 & 0 \\
C_{3333} & 0 & 0 & 0 & 2C_{2323} & 0 \\
\text{sym.} & 2C_{2323} & 0 & C_{1111} - C_{1122}
\end{bmatrix} B_\alpha \otimes B_\beta. \quad (19)$$

The orthonormal basis $B_\alpha$ of symmetric second-order tensors is defined by

$$B_1 = e_1 \otimes e_1, \quad B_4 = \frac{\sqrt{2}}{2} (e_2 \otimes e_3 + e_3 \otimes e_2),$$

$$B_2 = e_2 \otimes e_2, \quad B_5 = \frac{\sqrt{2}}{2} (e_1 \otimes e_3 + e_3 \otimes e_1),$$

$$B_3 = e_3 \otimes e_3, \quad B_6 = \frac{\sqrt{2}}{2} (e_1 \otimes e_2 + e_2 \otimes e_1). \quad (20)$$

For homogenizing the effective elastic properties from the submicro level to the micro level, the stiffness $\tilde{C}$ and the PODF have to be used (see Eq. (19)). Since $\tilde{C}$ is not known, the elastic constants of graphite (G) and pyrolytic graphite (PyG) will be considered. The corresponding elastic constants are given in Table 2.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\tilde{C}_{1111}$ [GPa]</th>
<th>$\tilde{C}_{3333}$ [GPa]</th>
<th>$\tilde{C}_{2323}$ [GPa]</th>
<th>$\tilde{C}_{1122}$ [GPa]</th>
<th>$\tilde{C}_{1133}$ [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blakslee et al. [7]</td>
<td>PyG</td>
<td>1060.0</td>
<td>36.5</td>
<td>4.0</td>
<td>180.0</td>
</tr>
<tr>
<td>Michel and Verberck [21]</td>
<td>G</td>
<td>1211.3</td>
<td>36.8</td>
<td>4.18</td>
<td>275.5</td>
</tr>
</tbody>
</table>

### 4.2 First-order bounds

The most simple bounds are the arithmetic and the harmonic mean of the local stiffness tensors, which were first suggested by Voigt and Reuss [26, 30]. For uniform microstructures, where the planes differ only with respect to their orientation, these bounds can be written as

$$C^V = \int_{SO(3)} f(Q) C(Q) \, dQ = \int_{SO(3)} f(Q) Q \ast \tilde{C} \, dQ \quad (21)$$

and

$$S^R = \int_{SO(3)} f(Q) S(Q) \, dQ = \int_{SO(3)} f(Q) Q \ast \tilde{S} \, dQ. \quad (22)$$

The arithmetic and the harmonic mean correspond to the assumption of homogeneous strain and stress fields, respectively (see, e.g., [19]). These approaches give upper and lower bounds for the strain energy density. They represent the best bounds if the orientation distribution is the only microstructural information available. For discrete orientation data, the two bounds can be represented by weighted sums of the local elasticity tensors analogous to Eq. (9).

### 4.3 Second-order bounds

Since the simple bounds are generally rather inaccurate, we consider in the following Hashin-Shtrikman bounds which are of second-order in the phase-contrast [23, 24, 29, 33]. The effective stiffness tensor is given by

$$\bar{C} = \langle CA \rangle, \quad (23)$$
where the localization tensor has to be determined by
\[
A = (I^S + P_0 \delta C)^{-1} \left\langle (I^S + P_0 \delta C)^{-1} \right\rangle^{-1}, \quad \delta C = C - C_0.
\] (24)

\(C_0\) and \(P_0\) denote the stiffness tensor and the polarization tensor of the comparison material, respectively. If the comparison stiffness satisfies
\[
Q \ast \tilde{C} - C_0 \leq 0, \quad \forall Q \in SO(3),
\] (25)
then an upper bound is obtained. A comparison stiffness with
\[
Q \ast \tilde{C} - C_0 \geq 0, \quad \forall Q \in SO(3)
\] (26)
yields a lower bound.

For microstructures with two-point probability functions with ellipsoidal symmetry, the polarization tensor is given by
\[
P_0 = \frac{1}{4\pi \sqrt{\det(A)}} \int_{||n||=1} \frac{H(n)}{(n \cdot An)^{3/2}} \, dc.
\] (27)
with \(H = I^S (N \otimes (n \otimes n)) I^S, N = K^{-1},\) and \(K = C_0[[n \otimes n]].\) The second-order tensor \(A\) describes the morphology of the microstructure. Its eigenvectors are equal to the anisotropy directions of morphologic anisotropy, which for microstructures with ellipsoidal symmetry can be orthotropic, transversely isotropic, or isotropic.

Without loss of generality, the comparison material can be chosen to be isotropic (see, e.g., [22]), i.e.,
\[
C_0 = C' = k_1 P'_1 + k_2 P'_2,
\] (28)
with
\[
P'_1 = I \otimes I/3, \quad P'_2 = I^S - P'_1.
\] (29)
For isotropic two-point statistics, i.e., \(A = I\) holds. Then \(P_0\) is given by
\[
P_0(C_0) = \frac{1}{4\pi} \int_{||n||=1} H(C_0, n) \, dn.
\] (30)
In this case the polarization tensor \(P_0\) is given by (see, e.g., [8])
\[
P_0' = p_1 P'_1 + p_2 P'_2, \quad p_1 = \frac{1}{k_1 + 2k_2}, \quad p_2 = \frac{2}{3k_2} \frac{k_1 + 3k_2}{k_1 + 2k_2}.
\] (31)
For \(A = I\) the anisotropy of the Hashin-Shtrikman bounds results completely from the anisotropy of the PODF. In this case the bounds can be represented as
\[
\tilde{C} = \langle CA \rangle = \int_{SO(3)} f(Q) C(Q) A(Q) \, dQ,
\] (32)
with the localization tensor
\[
A(Q) = (I^S + P_0 \delta C(Q))^{-1} \left\langle (I^S + P_0 \delta C(Q))^{-1} \right\rangle^{-1}, \quad \delta C(Q) = C(Q) - C'_0,
\] (33)
where the reference stiffness tensor \(C'_0\) satisfies one of the inequalities (25) and (26). With the transversely isotropic elastic constants given in Table 2 and the assumption of isotropic two-point statistics, the eigenvalues \(k'_1, k'_2\) and \(k'_1, k'_2\) of \(C_0\) are determined numerically by solving the extremal problems in Eq. (25) and (26) for the Hashin-Shtrikman upper and lower bounds, respectively (see Table 3).
e.g., [3]), it is sufficient to plot a contour line of the elastic modulus in a plane that contains the symmetry axis (see Fig. 15).

In Fig. 15a,b, the first- and second-order bounds of the elastic properties for HT PyC of Fig. 2a are given using the elastic constants of G and PyG, respectively. Due to the rotationally symmetric distribution of the c-axes of the graphene planes, the micro-effective behavior of PyC is transversely isotropic. For a graphical representation of the elastic properties (see, e.g., [21]), the average value $E_{\text{HS-M}} = \frac{E_{\text{HSU}}(\beta) + E_{\text{HSL}}(\beta)}{2}$ is defined and quantifies approximately the amount of anisotropy.

By comparing the Voigt bound and the Hashin-Shtrikman upper bound (V-HSU), the average value $\zeta_1 = \int_0^{90} E/V(\beta) / E_{\text{HSU}}(\beta) \, d\beta / \pi$ is found to be 1.48. Analogously, for the Hashin-Shtrikman lower bound and the Reuss bound (HSL-R), the average value $\zeta_2 = \int_0^{90} E_{\text{HSL}}(\beta) / E_R(\beta) \, d\beta / \pi$ is 1.52 and moreover very similar to the average value $\zeta_1$ (see Table 4). Since the elastic properties of G and PyG show only minor differences (see Table 2), the corresponding bounds are also similar, as expected.

Furthermore, it can be concluded that the estimation of the micro-effective properties implies a significant uncertainty since the absolute differences between the first- and second order bounds (both for G and PyG as comparison medium) are quite large. This is due to the high amount of anisotropy of the materials. Using $\Delta E_{\text{HSM}}$ of the effective elastic properties, the reduction of anisotropy due to the distribution of the orientation of the graphene planes in comparison to the elastic properties of G [21] is about 81%.

Young’s moduli corresponding to the different estimations (Voigt, Reuss, HSL, HSU, and HS-Mean) of MT and LT are shown in Fig. 16a,b, respectively. The data of the effective Young’s moduli for MT and LT PyC are given in Table 4. Due to the similar elastic properties of G and PyG, the bounds of MT and LT are given based on the constants of G, only. The results show that the effective bounds of MT and LT are very close which can be explained by the similar values of the concentration parameters $\kappa$ in the PODF (see Table 1). That means that MT and LT PyC possess a similar mechanical

<table>
<thead>
<tr>
<th>Material</th>
<th>$k_{11}$ [GPa]</th>
<th>$k_{22}$ [GPa]</th>
<th>$k_{12}$ [GPa]</th>
<th>$k_{23}$ [GPa]</th>
<th>$\Delta E_{\text{HSM}}$ [GPa]</th>
<th>$\zeta_1$ [-]</th>
<th>$\zeta_2$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blakslee et al. [7]</td>
<td>PyG</td>
<td>1537.77</td>
<td>880.0</td>
<td>92.62</td>
<td>8.0</td>
<td>1.48</td>
<td>1.52</td>
</tr>
<tr>
<td>Michel and Verberck [21]</td>
<td>G</td>
<td>2323.05</td>
<td>935.8</td>
<td>90.62</td>
<td>8.36</td>
<td>1.48</td>
<td>1.52</td>
</tr>
</tbody>
</table>

Table 3: Data of the effective Young’s moduli for HT, MT, and LT PyC.
behavior. One also finds that the amount of anisotropy of the different textures is ordered, i.e.,
\[ \Delta E_{HSM}^{HT} > \Delta E_{HSM}^{MT} > \Delta E_{HSM}^{LT}, \]
which consistently corresponds to
\[ \kappa_{HT} > \kappa_{MT} > \kappa_{LT} \]
in Table 1 due to the different degrees of anisotropy of the textures. The \( \zeta_1 \) and \( \zeta_2 \) for MT and LT are equal to the corresponding data in the case of HT. Therefore, the ratios for V-HSU and HSL-R are independent of the textures. Compared to the elastic constants of G, the reduction of anisotropy for MT and LT are 90% and 92%, respectively. In Table 4, the relationships \( E_{HSM}^{HT}(\beta = 0^\circ) < E_{HSM}^{MT}(\beta = 0^\circ) < E_{HSM}^{LT}(\beta = 0^\circ) \) and \( E_{HSM}^{HT}(\beta = 90^\circ) > E_{HSM}^{MT}(\beta = 90^\circ) > E_{HSM}^{LT}(\beta = 90^\circ) \) can be concluded due to a smaller degree of anisotropy corresponding to a flat distribution of \( E_{HSM}(\beta) \).

5 Conclusions

In the present paper, the orientation distribution of the graphene layers has been modeled by using the von Mises-Fisher distribution, since the mean orientation of the graphene layers is according to the growth direction of the PyC layers and all orientations stochastically distribute around the mean orientation in the image plane. The probability density function \( \tilde{f}_\kappa(\alpha, \gamma) \) for the orientation of the projections of the graphene planes, which is induced by the von Mises-Fisher distribution, is obtained in analytical form containing the concentration parameter \( \kappa \) of the von Mises-Fisher distribution, the mean orientation angle \( \gamma \) of the layer planes, and the orientation angle \( \alpha \) of the layer plane.

Combining FT methods with a LoG filter and line integration techniques for given HRTEM images of the different PyC textures HT, MT, and LT, the distributions of the projected orientation of the graphene layers in the image plane have been numerically obtained. The unknown parameters \( \kappa \) and \( \gamma \) have then been uniquely determined by the Maximum-Likelihood-method separately for the three textures HT, MT, and LT, yielding \( \kappa_{HT} > \kappa_{MT} > \kappa_{LT} \). However, due to the small dimensions of the HRTEM images used (50 × 50 nm²), the quality of these parameter estimations might be improved based on larger HRTEM sections.

By observing the homogenization results of the linear elastic properties of HT, MT, and LT PyC, the changes in the mean values of the first- and second-order bounds of MT and LT are consistently similar. HT PyC contains the most anisotropic elastic properties corresponding to the largest \( \kappa \).

In summary, by assuming an identical mechanical behavior within the area of the same oriented graphene layers, the homogenization of the linear elastic properties of PyC has been performed under a continuum hypothesis. A continuous displacement field is assumed implying that the microelastic behavior is completely determined by bulk properties. The first- and second-order bounds are with uncertainties in the local values of elastic properties due to the high amount of anisotropy of the reference materials. The anisotropy is significantly reduced from HT to MT and LT by taking into account the distribution of the orientation of the graphene planes. Compared with the elastic material properties of graphite, the reductions of the anisotropy are 81%, 90%, and 92% for HT, MT, and LT, respectively.

For estimating the elastic properties of heterogeneous materials generally a hierarchy of bounds can be used [15]. First-order bounds require only volume fraction information, i.e. the one-point correlation function, second-order are based on
two-point correlation functions. The determination of higher-order correlation functions is a difficult task since it requires extensive microstructural information. In the present model approach only the three-dimensional orientation distribution of c axes is determined based on HRTEM images. For a reliable estimate of the second-order correlation function sections of images would have to be analyzed. Since such data is not available, we assume isotropic two-point statistics and use the Hashin-Shtrikman scheme which specifies the two-point statistics in terms of the one-point statistics [24].

Although second-order bounds have been computed, the estimation of the effective properties on micro level shows quite large uncertainties. The gap between the bounds can be explained by the large amount of elastic anisotropy. This anisotropy in combination with different microstructures implies a wide range of possible micro-effective properties. Only the application of higher than second-order bounds may reduce this gap thereby requiring additional morphological information. The determination of this information is far beyond the scope of this work.

It is known that even for the Voigt and the Reuss bound the bounds represent extreme cases of morphological anisotropies. Furthermore, numerical results show that higher order bounds for isotropic higher-order correlation functions are approaching the mean value of the bounds [4]. This has motivated the use of the mean value of the Hashin-Shtrikman bounds as an approximation of the real micro properties.

Comparing \( \Delta E_{HSM} \) of HT PyC with the measurement of the Young’s moduli of PyC by Gebert et al. [13], the predictions in this work are about 14 times more stiffer than the data of Gebert et al. [13]. This is certainly due to the large differences of the sample sizes considered: Gebert et al. [13] investigated PyC specimen with \( 15 \times 15 \text{ mm}^2 \) size, whereas the HRTEM images used in this work carry only the information within the area of size \( 50 \times 50 \text{ nm}^2 \). For the specimen on the macro level, the elastic properties will be expected to be less stiff than on the micro level due to macro defects and porosities of the samples.

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