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CarbX: a program for the evaluation of wide-angle X-ray scattering data of non-graphitic carbons

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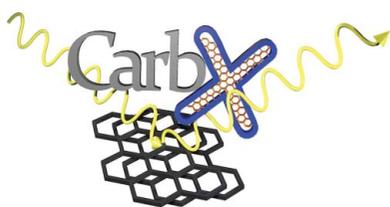
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CarbX is an open-source program designed for the analysis of wide-angle X-ray scattering (WAXS) data of non-graphitic carbons (NGCs). As knowledge of their microstructure is crucial for tuning desired properties, an ‘easy-to-use’ analysis tool is essential for effective research in this field. Using *CarbX* one can retrieve up to 14 microstructural parameters from a single WAXS pattern without having to master the associated complicated mathematics. *CarbX* was developed to serve as a convenient graphical user interface, translating a complex evaluation algorithm introduced by Ruland & Smarsly [*J. Appl. Cryst.* (2002), **35**, 624–633] into software which can be operated by non-experts. Besides the core functionality of displaying data and manually fitting WAXS curves by user-editable parameters, *CarbX* offers additional features such as visualization of the deviation between data and fit, the possibility to choose the wavelength used in the measurement, and automatic fitting (using Wolfram *Mathematica*). One of the key features of the comfortable usability is the functionality to display templates. This allows the user to visually compare measurement data with typical types of NGC WAXS curves which are presented graphically around the measurement data. The authors believe that this program will provide a useful tool for scientists dealing with the characterization of NGCs.

1. Introduction

Non-graphitic carbons (NGCs) are an important and promising material class of carbon for current and future applications in research, development and industrial applications. Besides their usage as molecular sieves, in catalyst materials and as filters, NGCs are applied as active electrode materials and as conductive additives in batteries. Research in the field of future generations of batteries and accumulators thus includes optimization of carbons through variation of their structure on the micrometre and nanometre scale, referred to here as ‘microstructure’. By IUPAC definition (Fitzer *et al.*, 1995), NGCs are classified as carbon exhibiting only long-range order in the two-dimensional hexagonal carbon lattice but no measurable crystallographic order in the third direction, with the sp^2 polyaromatic layers being stacked nearly parallel to one another.

Since the class of NGCs comprises a wide variety of materials differing in the size and lattice distortions of the graphene stacks, it is generally desirable to know the corresponding atomic structural parameters. Such knowledge is required both for tuning the production process to ensure that a material with the desired properties is obtained and for linking macroscopic properties like electrical conductivity, friction resistance and mechanical strength to the microstructure of the material. A promising approach for the determination of



the microstructure of NGCs is the acquisition of wide-angle X-ray scattering (WAXS) data, assuming a polycrystalline structure, and subsequent fitting of the whole WAXS curve using a suitable model. In this respect, such a fitting approach is also well known in the Rietveld refinement of powder X-ray diffraction data in the case of crystalline materials. Shi *et al.* (1993) applied such a fitting approach to carbons as early as 1993.

In 2002, Ruland and Smarsly introduced a novel approach for the WAXS analysis of NGCs by fitting WAXS data using suitable functions (Ruland & Smarsly, 2002). These functions describe the theoretically expected WAXS curve for a given set of microstructural parameters. Thereby the applicability of this approach for selected samples was demonstrated. Recently, the approach of Ruland and Smarsly was applied to the WAXS data of different types of carbons, proving the applicability for carbons of different size and order of the graphene stacks (Zickler *et al.*, 2006; Adelhalm *et al.*, 2012). Although the fitting approach of Ruland and Smarsly is based on a physically meaningful structural model (see Faber *et al.*, 2014a,b) and was shown to provide useful insights into the microstructure of carbons, the underlying model suffers from its elaborate mathematical formulation, which is probably the reason why the approach has not been used widely. In the analysis given by Ruland & Smarsly (2002) the model was first implemented in *gnuplot* (<http://www.gnuplot.info/>); this was followed by an implementation (Faber *et al.*, 2014a,b; Einert *et al.*, 2015) in Wolfram *Mathematica* (<https://www.wolfram.com/mathematica/>), making the analysis more convenient but still challenging for users inexperienced in programming. Motivated by the intention to facilitate the analysis of WAXS-based analysis of NGCs, we have developed the program *CarbX*, which is introduced in the following. The main development objective is to create an ‘easy-to-use’ computer program for the microstructural analysis of NGCs based on the model proposed by Ruland & Smarsly (2002).

In this paper, the first publicly available version of *CarbX* is presented. The primary intent is to provide a convenient graphical user interface (GUI), which translates the approach of Ruland and Smarsly into a program that can be used by researchers without profound knowledge of mathematical programming. For this purpose, a template functionality is included, allowing the user to choose a suitable template, *i.e.* reliable initial values for the parameters, from a graphical display of typical NGC WAXS curves. This significantly simplifies fitting of NGC WAXS data. The second major objective lies in the creation of a software tool that allows for the implementation of variable fitting routines, since the choice of a suitable nonlinear fitting procedure is crucial for a meaningful analysis of the WAXS data. Therefore, the code of *CarbX* is intentionally made public to be modified and improved by other researchers, especially with respect to suitable fitting routines. As an example, in the present publication we describe how to use the nonlinear fitting routing in *Mathematica* by linking it to *CarbX*.

In the following section, the theoretical basis of the approach of Ruland and Smarsly is summarized, and this is

complemented by a discussion on the handling of the acquired WAXS data. Subsequently, the technical details of *CarbX* as well as the usage will be described. In addition, the validity of *CarbX* is demonstrated in three different ways utilizing WAXS data of representative NGCs. First, the parameters given in the corresponding publications were typed into *CarbX* and the fits depicted there compared with those produced by *CarbX*. Second, ‘manual fitting’, *i.e.* varying the parameters by hand, of the data was performed. Third, automatic fitting was performed by coupling *CarbX* with the nonlinear fitting routine of *Mathematica*. For the last step the values of the parameters obtained in the second step are used as initial values. Finally, the resulting structural parameters were compared with the analysis by the previously applied methods.

2. Modelling the WAXS data of NGCs

In *CarbX*, the modelling of the WAXS data of NGCs is based on the algorithm of Ruland & Smarsly (2002), taking advantage of the enhancement described by Faber *et al.* (2014a,b) as well as some further development to be described below and in the supporting information. The theoretically observable intensity is proportional to the sum of coherent scattering I_{coh} and incoherent scattering I_{incoh} :

$$I_{\text{theoretical}} \propto (I_{\text{coh}} + I_{\text{incoh}}). \quad (1)$$

The coherent scattering intensity results from the interlayer and intralayer scattering as well as the scattering from unorganized nitrogen c_{N} and oxygen c_{O} impurities. In addition, the scattering from unorganized carbon c_{un} as well as the anisotropy of the atomic scattering factor for carbon perpendicular to the graphene sheets $f_{\text{C,perp}}$ has to be considered. The slight change of the tabulated form factor for carbon caused by this anisotropy is accounted for by the empirical parameter Δ_{an} . As the atomic scattering factor for carbon parallel to the graphene sheets $f_{\text{C,para}}$ is considered to be isotropic, its value equals the tabulated value for the atomic scattering of carbon. With these assumptions, I_{coh} is given by

$$I_{\text{coh}} = (1 - c_{\text{un}})(f_{\text{C,perp}}^2 I_{\text{inter}} + f_{\text{C,para}}^2 I_{\text{intra}}) + c_{\text{un}} f_{\text{C,para}}^2 + c_{\text{N}} f_{\text{N}}^2 + c_{\text{O}} f_{\text{O}}^2. \quad (2)$$

Within the model of Ruland and Smarsly I_{inter} describes the interlayer scattering and depends on the parameters L_{c} , κ_{c} , a_3 , $a_{3,\text{min}}$, σ_3 , u_3 , η , I_{cc} , q . I_{intra} describes the intralayer scattering and depends on L_{a} , κ_{a} , I_{cc} , σ_1 , q . An explanation of the parameters is given in Fig. 1. Further details can be found in the supporting information and recent publications (Ruland & Smarsly, 2002; Faber *et al.*, 2014a,b).

The incoherent scattering intensity I_{incoh} is given by the theoretical intensity of the Compton scattering $I_{\text{com,C}}$. The theoretical values are obtained by interpolation of the values given, for example, in *International Tables for X-ray Crystallography* (Ruland & Smarsly, 2002), as depicted in Fig. 2. If primary and/or secondary monochromatization is applied,

specific correction factors have to be taken into account. For primary monochromatization the correction terms are the Breit–Dirac recoil factor, recoil, and the factor for specific absorption of Compton scattering, Q_{abs} (Ruland & Smarsly, 2002). As a standard diffractometer uses primary mono-

chromatization, both factors are always taken into account for the calculations performed in *CarbX*. For secondary monochromatization the attenuation of the Compton scattering due to finite resolution of the monochromator has to be taken into account (Ruland & Smarsly, 2002) by the correction term Q .

These factors are defined in the supporting information. In summary, in *CarbX*, I_{incoh} is defined as follows, with Q as an optional factor:

$$I_{\text{incoh}} = I_{\text{com,C}} \text{recoil } Q_{\text{abs}} Q. \quad (3)$$

Further details about incoherent scattering can be found in the work of Ruland (1961, 1964).

Additionally, for a correct description of theoretical scattering intensity, the polarization and absorption have to be considered by including the polarization factor P and the absorption factor A , respectively. Furthermore, correction of the background by the normalization constant k , the tuning of the overall slope of the scattering/fit curve by the factor gFact and the consideration of the possible use of an automatic collimator by the factor AutoColl are required for a correct description of the theoretical scattering intensity. For these reasons, the theoretical scattering intensity $I_{\text{theoretical}}$ used in *CarbX* is defined as

$$I_{\text{theoretical}} = (1/\text{AutoColl}) (\text{gFact}) \times k A P (I_{\text{coh}} + I_{\text{incoh}} Q). \quad (4)$$

The factors $1/\text{AutoColl}$, gFact, A and Q are optional and thus neglected if not selected by the user. If deselected, the factors are set to the fixed value 1. The equations for the correction/tuning factors are given in the supporting information.

In rows 1–24 of Table 1 the parameters to be entered in *CarbX* for the calculation of the fitted curve are listed. The Y values of the curve are calculated as the logarithm of the theoretically observable intensity corrected by two parameters, const_1 and const_2 :

$$I_{\text{obs}} = \log_{10}(I_{\text{theoretical}} + \text{const}_1) + \text{const}_2. \quad (5)$$

These two parameters are used as in many cases a non-constant background is observed, which cannot be considered by merely shifting the fitted curve vertically (here realized with const_2).

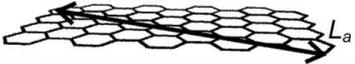
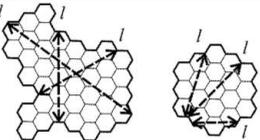
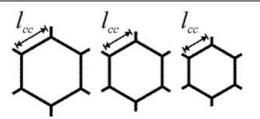
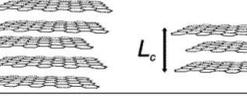
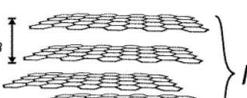
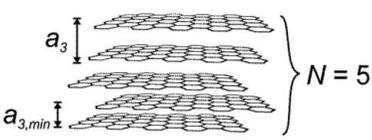
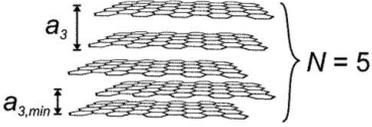
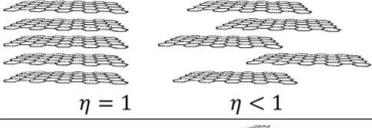
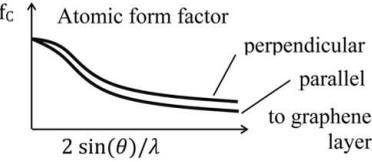
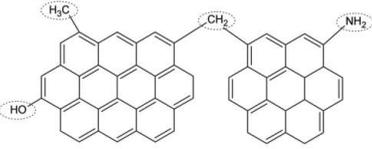
	Parameter	Denotation	Explanation
Layer structure	L_a^b	Average graphene layer extent	
	$\langle l \rangle^b$	Average chord length	
	κ_a^b	Polydispersity of chord length l	
	l_{CC}	Average C-C bond length	
	σ_1	Standard deviation of the first-neighbor distribution	
Layer stacking	L_c^c	Average stack height	
	κ_c^c	Polydispersity of stack height	
	a_3	Average interlayer spacing	
	$a_{3,\text{min}}$	Minimum of interlayer spacing	
	σ_3	Standard deviation of interlayer spacing	
	$\langle N \rangle^c$	Number of graphene layers per stack	
	u_3	Parameter of thermal motion	
	η	Homogeneity of the stacks	
	q	Parameter of preferred orientation	
	Δ_{an}	Parameter of anisotropy of the atomic form factor of carbon	
Impurities	c_{un}	Concentration of unorganized carbon	
	c_N	Concentration of unorganized nitrogen	
	c_O	Concentration of unorganized oxygen	

Figure 1

Overview of the 14 microstructural parameters of non-graphitic carbons obtainable by fitting the WAXS data according to the model of Ruland & Smarsly (2002) and further parameters considered for correct modelling. The represented parameters are not mathematically independent. Reprinted with permission from Faber *et al.* (2014a) [copyright (2014) American Chemical Society]. ^bThese parameters are dependent, since the shape factors ν and α , which describe a gamma distribution, are used for their calculation. ^cThese parameters are dependent, since the shape factors μ and β , which describe a gamma distribution, are used for their calculation.

Table 1
Overview of the parameters used in and calculated by *CarbX*.

Row number	Parameter (symbol)	Parameter (in <i>CarbX</i>)	Meaning
01	c_{un}	cno	Concentration of unorganized carbon
02	μ	mu	Shape factor for calculation of $\langle N \rangle$, N^* , L_c , κ_c
03	β	beta	Shape factor for calculation of $\langle N \rangle$, N^* , L_c , κ_c
04	a_3	a3	Average interlayer spacing (Å)
05	Δ_{a_3}	da3	Difference between a_3 and $a_{3\text{min}}$ (Å)
06	σ_3	sig3	Standard deviation of interlayer spacing (Å)
07	u_3	u3	Parameter of thermal motion (Å)
08	η	eta	Homogeneity of the stacks
09	ν	nu	Shape factor for calculation of L_a , $\langle l \rangle$, κ_a
10	α	alpha	Shape factor for calculation of L_a , $\langle l \rangle$, κ_a
11	σ_1	sig1	Standard deviation of the first-neighbour distribution
12	l_{cc}	lcc	Average C–C bond length (Å)
13	q	q	Parameter of preferred orientation
14	c_{N}	cN	Concentration of unorganized nitrogen
15	c_{O}	cO	Concentration of unorganized oxygen
16	Δ_{an}	dan	Parameter of anisotropy of the atomic form factor of carbon
17	k	k	Normalization constant: $I_{\text{obs}} = \log_{10}(kI_{\text{fit}} + \text{const}_1) + \text{const}_2$
18	const_1	const1	Vertical shift of the fitted curve: $I_{\text{obs}} = \log_{10}(kI_{\text{fit}} + \text{const}_1) + \text{const}_2$
19	const_2	const2	Vertical shift of the fitted curve: $I_{\text{obs}} = \log_{10}(kI_{\text{fit}} + \text{const}_1) + \text{const}_2$
20	g	g	Tuning of gradient/slope by $\exp(g_s)$: $I_{\text{fit}} \exp(g_s)$
21	μ_{ab}	mue_ab	Absorption factor for correction of absorption by $I_{\text{fit}}A$, or of the correction of the data themselves, included in Dz, D2ttx, Lambert–Beer
22	p	p	Parameter for correction of absorption for measured curve by the pragmatic approach
23	R	R	Parameter for correction of positions according to D2ttx
24	t	t	Parameter for correction of positions according to D2ttx
25	L_a	La	Average graphene layer extent (Å) calculated by $(\nu + 1)/\alpha$
26	$\langle l \rangle$	$\langle l \rangle$	Average chord length (Å) calculated by ν/α
27	κ_a	kapa	Polydispersity of chord length l calculated by $1/\nu$
28	$\langle N \rangle$	$\langle N \rangle$	Average number of graphene layers per stack as given by μ/β
29	N^*	N*	Average number of graphene layers per stack as given by $(\mu + 1)/\beta$
30	L_c	Lc	Average stacking size (Å) calculated by $a_3(\mu + 1)/\beta$
31	κ_c	kapc	Polydispersity of stack height calculated by $1/\mu$
32	$a_{3,\text{min}}$	a3min	Minimum of interlayer spacing (Å) calculated by $a_3 - \Delta_{a_3}$
33	ε_3	eps3	Disorder of graphene layers due to local strains calculated by $\Delta_{a_3}/a_{3,\text{min}}$
34	κ_r	kapr	Polydispersity of the radius of the layers calculated by $3\pi^2(1/\nu + 1)/32 - 1$

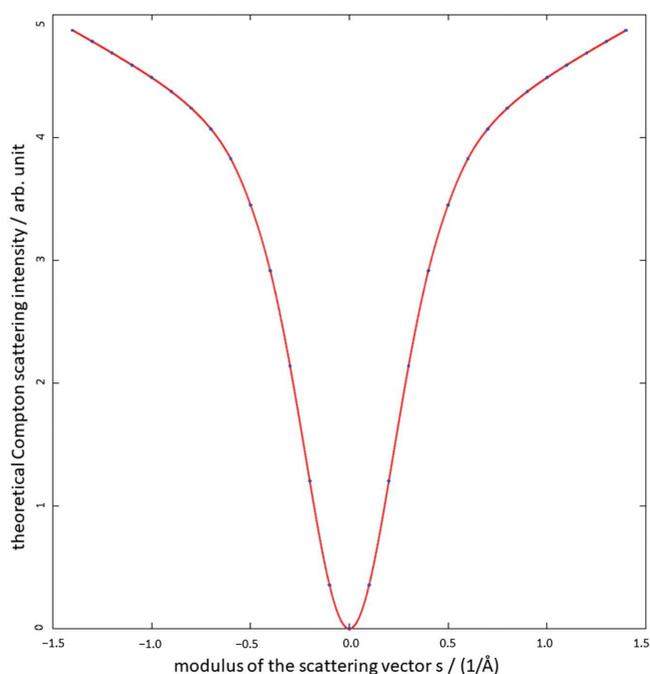


Figure 2
Interpolation of the theoretical Compton scattering intensity of carbon (red) along with the data points used for the interpolation (blue).

Thus the additional factor const_1 was established and has proven itself useful since then. Note that the factors AutoColl, A and Q also affect the background and thus should be chosen accordingly before using const_1 and const_2 to consider a background.

Most of these parameters have direct physical meaning. By contrast, several of the parameters belonging to the gamma functions (μ , β , ν , α) are related to the structural parameters [see also supporting information; for further details refer to Faber *et al.* (2014b) and Ruland & Smarsly (2002)]. The shape factors are used for calculation of structural parameters that are not directly entered in the *CarbX* program (L_a , $\langle l \rangle$, κ_a , $\langle N \rangle$, N^* , L_c , κ_c , $a_{3,\text{min}}$, ε_3 , κ_r). These parameters are listed in rows 25–34 of Table 1 and can be accessed by exporting a result parameter file in *CarbX*. The result file contains all parameters given in Table 1. In addition, some parameters are factors used in the correction/tuning terms described above or for correcting the raw measurement data (g , μ_{ab} , p , R , t , given in rows 20–24 of Table 1). The parameters const_1 , const_2 (given in lines 18 and 19 of Table 1) are used for empirical background correction. The terms for correcting the raw measurement data regarding position of the reflections (Dz and D2ttx) and absorption by the sample (Lambert–Beer and the pragmatic approach) are given in the supporting information.

3. Technical details of the *CarbX* program

The current version of *CarbX* is written in the C++ programming language using the Qt application framework version 5.7.1 (<http://qt.io>). Furthermore, the Qt Widgets for Technical Applications Library (Qwt) version 6.1.3 is utilized (*CarbX* is based in part on the work of the Qwt project; <http://qwt.sf.net>). In addition, the Wolfram Symbolic Transfer Protocol (WSTP) library (<http://wolfram.com/wstp/>) and some routines from the book *Numerical Recipes in C* (Press *et al.*, 2000) are used. The DLL files required to run *CarbX* are included in the downloadable package. The file `wstp32i4.dll`, included in the ZIP archive of the program, is part of WSTP (Copyright 2015 Wolfram Research Inc.) and is distributed by Torben Pfaff with permission of the author of WSTP. Any unauthorized use or distribution is strictly prohibited. *CarbX* requires at least Windows 7 as operating system, but Windows 10 is recommended. *CarbX* should run on any machine that is capable of running Windows 7 or 10, though some calculation steps may require a significant amount of time on processors older than Intel's Core 2 family or AMD's Athlon X2 for AM2 sockets. Furthermore, a certain amount of RAM is necessary for *CarbX* to run properly, depending on the size of the data file. Thus, at least 2 GB of RAM and at least a dual-core CPU with not less than 2 GHz are recommended.

3.1. Third-party components used in *CarbX*

The following sections provide a brief characterization of the third-party components used in *CarbX*. For further details refer to the web site of the corresponding software package.

3.1.1. Qt. Qt is a development tool for cross-platform C++ applications with a main focus on GUIs. Qt contains classes for various purposes, including easy-to-use non-primitive data types, file access, and dialogues to display messages or select files and folders. Qt comes with an integrated development environment, which allows for relatively easy creation of a GUI and convenient programming of source code. Moreover, Qt provides tools for straightforward translation of an application's captions, dialogue messages *etc.*

3.1.2. Qwt. The Qwt library includes, among other widgets, the option to display two-dimensional data points in the form of a plot. Several options are available, including automatic scaling of axes, a grid, spline interpolation of data points and the layout of the displayed curves. In general, the Qwt library provides a variety of input and display widgets for technical and/or scientific applications.

3.1.3. WSTP library. Using the WSTP library, external programs can communicate with a local or remote *Mathematica* kernel using the Wolfram Symbolic Transfer Protocol. Thus, every computer program written in a supported language for a supported platform can utilize the kernel to



Figure 3

Screenshot of the main window of the GUI. It is divided into five sections, marked by Roman numerals. Section I is the menu bar, section II contains buttons for several purposes, section III the sliders to adjust the parameters, section IV the plot area and some options for the plot itself, and section V the options for the fit curve and raw measurement data correction as well as the wavelength selection.

perform calculations. The basic steps are to establish a connection to the kernel, send commands to it and retrieve the results. Both commands and results can be sent as strings or a variety of other data types, including integer, real, list and array. In addition, WSTP allows for calling functions provided in an external program using the Wolfram Language, e.g. in a Wolfram *Mathematica* notebook.

3.2. Main implementation structure of the program

The program is roughly divided into the core calculation routines, the GUI, program-wide used header files, and several classes for data storage, file access and automatic fitting. The core calculation routines are stored in one class and called from another class for easier access. The GUI has a class for each window and dialogue shown except for the standard dialogues. The remaining files and classes are described in detail in the supporting information.

3.3. Calculation routines

The calculation routines mainly use standard C++, particularly the functions provided by the header `<cmath>`. As the functions ‘cotangens hyperbolicus’ and ‘cosecans’ are not provided by this header, they are defined using the functions available in `<cmath>`. To calculate the interpolation functions as well as the gamma and hypergeometrical ${}_2F_1$ function, third-party routines from *Numerical Recipes in C* are used. As the whole program is developed using the Qt application framework, the calculations class also uses elements from Qt for file access. Further information regarding the calculation routines can be found in the supporting information.

3.4. GUI

The GUI is designed and created with Qt 5.4.1, which provides almost all needed widgets except an option for a plot. For this purpose the Qwt library provides a suitable plotting widget, which is used for displaying the different curves. The GUI is divided into a main window, two supporting windows and some dialogues, of which a few are special dialogues and therefore implemented by the author, whereas the other dialogues are standard dialogues, for example file access dialogues or message dialogues.

3.4.1. Main Window. The main window itself is also divided into five sections as shown in Fig. 3. The first section at the top is a menu bar with three menu points to access functions of a typical ‘file’ menu, the program settings and template-related functions (see below). The second section contains several



Figure 4
Screenshot of one slider to manipulate the parameters, in this case a_3 . The value can be set using the slider or directly or by adding/subtracting a user set value using the corresponding buttons. In addition, borders for the slider and thus the parameter value can be set.

buttons enabling the user to perform the actions required for manual and automatic fitting. The parameters for the curve fitting and correction of the raw data, however, are entered in section III using sliders, one of which is depicted in detail in Fig. 4. Both the measurement and data and the fitted curve are depicted in the plotting widget of section IV. In section V several options for the curve fitting and correction of the raw data as well as measurement parameters including the wavelength can be set. Further details about the elements of each section and their usage are given in the supporting information.

3.4.2. Supporting window to display the deviation. One supporting window contains elements for display of the deviation between the data and the fitted curve as well as manipulating the view of it and exporting the deviation data. A screenshot of this window is shown in Fig. 5. The equation used to calculate the deviation and a further description of this window are given in the supporting information.

3.4.3. Supporting window for automatic fitting. Another supporting window is included, allowing the user to manipulate the commands that are transmitted to *Mathematica* for automatic fitting, to perform automatic fitting, to preview the results of automatic fitting and to take the results over into the main window. A screenshot of this window is shown in Fig. 6. Elements, functions and usage of this window are further described in the supporting information.

3.4.4. Special dialogues. The special dialogues mentioned above are used to set the format of the raw data while loading

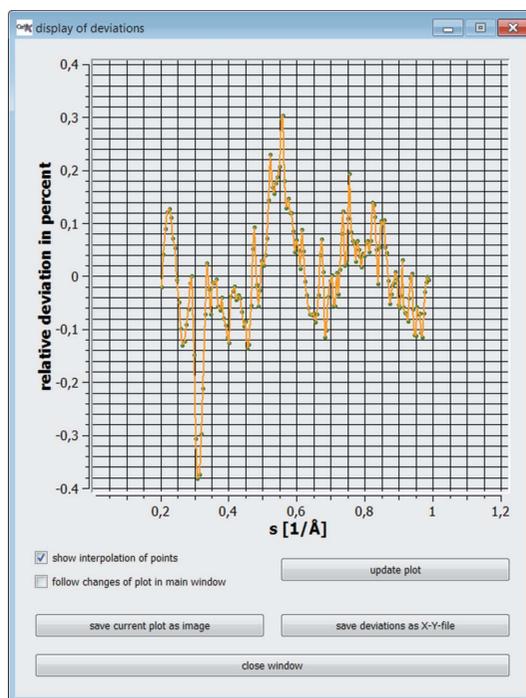


Figure 5
Screenshot of the supporting window to display the deviation between fit and measurement data. Besides the main plot area, this window contains some options for the plot, two buttons to export the deviation data and a button to close the window.

a data file, to set the program options (Fig. 7), to choose a template for the fitted curve (Fig. 8) and to enter the name of a template to be saved. A detailed description of the dialogues is given in the supporting information.

3.5. Key characteristics of *CarbX*

The key characteristics of *CarbX* are summarized below.

The program is written in C++ utilizing the following:

- (i) Qt application framework, version 5.4.1
- (ii) Qt widgets for technical applications, version 6.1.2
- (iii) GNU Scientific Library, version 1.8
- (iv) WSTP library
- (v) *Numerical Recipes*, version 2.11 in C

The system requirements are as follows:

- (i) Operating system: Microsoft Windows XP, 7 or 10
- (ii) 2 GHz dual-core CPU or better
- (iii) 2 GB of RAM or more

Note that *CarbX* will probably run on machines with less CPU speed and/or less RAM, but each calculation of the fitted curve and especially of the automatic fitting will be very time consuming.

4. Using the *CarbX* program

4.1. Setup and first start

In order to use the *CarbX* program, the program files have to be downloaded from <https://www.uni-giessen.de/CarbX-programme>. The downloaded ZIP archive has to be extracted

in an arbitrary but empty folder. As no further installation is required, the program can be started directly by executing the *CarbX.exe* file. After the initial start-up, some preferences should be chosen in the dialogue of the program options described above, and the wavelength should be defined. It is recommended to restart the program after applying the global settings to save the settings permanently on hard disk.

4.2. Loading of measurement data

To fit previously recorded WAXS data of an NGC sample, first an NGC file should be saved. Then the file containing the measurement data has to be loaded by using the corre-

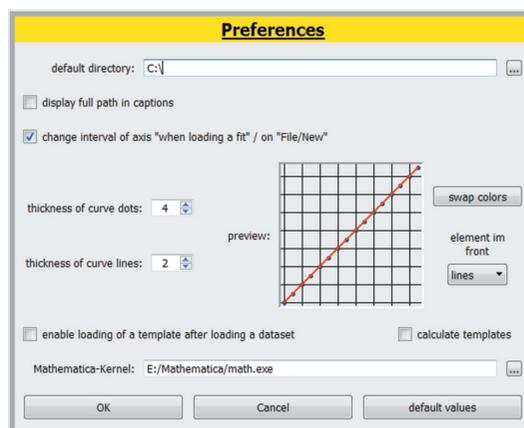


Figure 7
Screenshot of the preferences dialogue. In this dialogue several program preferences can be set. For setting the style of the plots, a preview is offered.

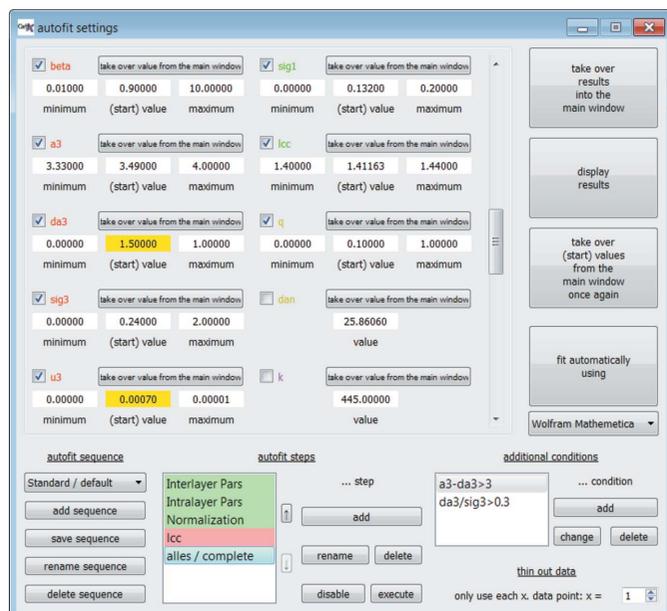


Figure 6

Screenshot of the supporting window to determine an autofit sequence and execute automatic fitting. This window contains elements for managing an arbitrary number of autofit sequences, determining the autofit steps for the chosen sequence, manipulating the (start) values for each step, executing the chosen sequence, and previewing and taking over the results of the automatic fitting.

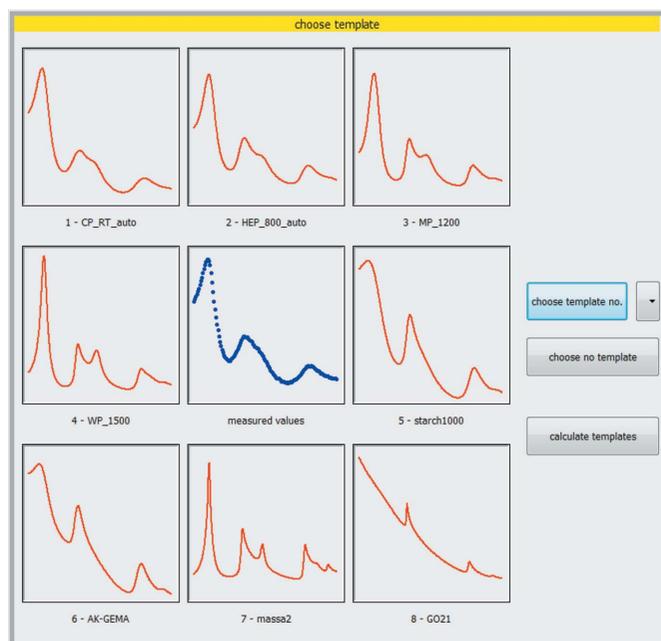


Figure 8

Screenshot of the dialogue to choose a template. The measurement data and the available templates are shown. The user can choose one of the available templates or no template.

sponding button and selecting the desired file to load. Once the right format of the data file, e.g. 'intensity linear versus $2\theta / ^\circ$ ', has been chosen and confirmed, the data should be displayed as a dotted curve in the plot section. If the format of the data file is not listed in the dialogue to choose the format of the data file,¹ the user has to convert the data file using an external tool before loading the file into *CarbX*. This also applies for correction of a known background, which must be subtracted from the raw measurement data using an external tool like *Origin* (<https://www.originlab.com/>) or *gnuplot* or a spreadsheet program. Correction of the background using an external tool is likewise required, if the background cannot be properly considered by the methods provided in *CarbX* (correction factors $1/\text{AutoColl}$, $g\text{Fact}$, A and Q , variation of normalization constant k , and/or variation of const_1 and const_2 for empirical background consideration). If a built-in method is used, only the input fields and slider structures necessary for the chosen method are enabled.²

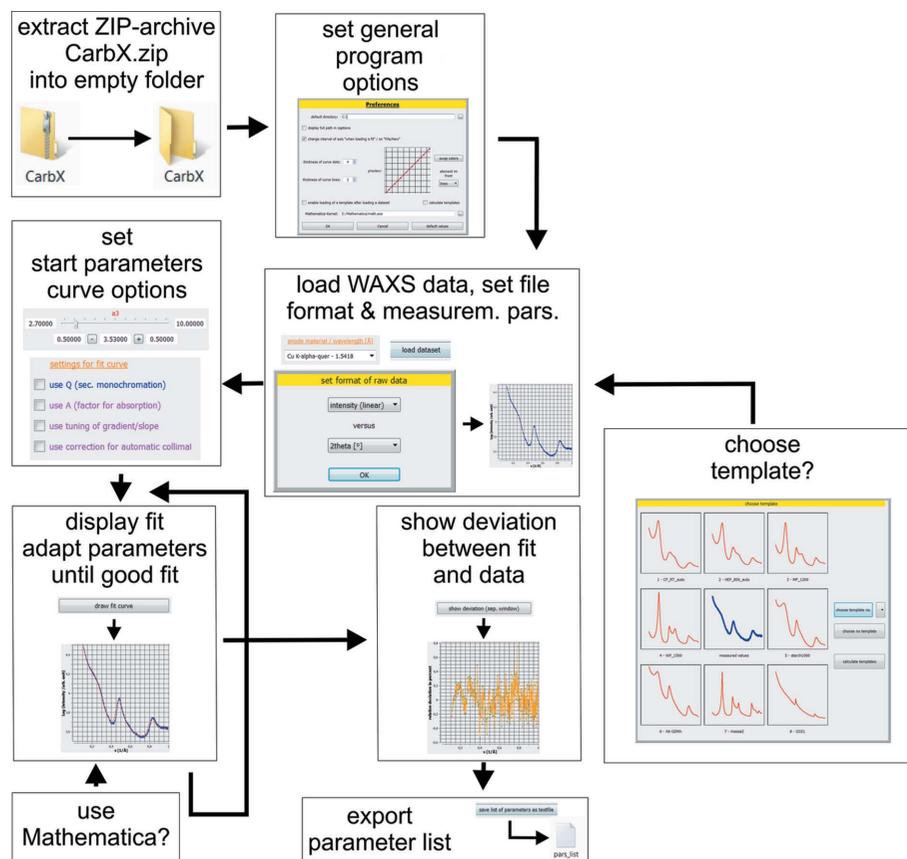


Figure 9
Flowchart of the steps required to fit WAXS data of NGCs using the *CarbX* program.

4.3. Manual (preliminary) fitting

After loading the measurement data, the user can display the preliminary/first fitted curve by clicking the corresponding button. If selected in the program preferences, a template can be chosen before this step. Once the fitted curve has been displayed, the parameters can be adjusted manually to match the fitted curve and the data as effectively as possible. It is recommend to first enter coarse values for each parameter using the particular text field and second to fine-tune each parameter using the plus/minus buttons and/or the slider. As using the slider consumes a lot of CPU time, only a part of the fitted curve should be displayed when using any of the sliders. For this purpose, the minimum/maximum of the horizontal axis has to be defined. Alternatively, the parameters can be adjusted while the fitted curve is not displayed or the option 'automatically recalculate fit curve' can be unset. Since some values of parameters (especially μ , a_3 , Δ_{a_3} , σ_3 and ν) can cause the program to crash, especially when the limits of the parameters are changed, the NGC file should be saved periodically. As for the correction of

the raw measurement data, *CarbX* also provides some methods to consider the measurement setup used ($1/\text{AutoColl}$ and Q), as well as $g\text{Fact}$ and A which correct the fitted curve as described above. After the method has been chosen, only the necessary input fields and slider structures are enabled (see footnote 2). As some correction methods cannot be used together, choosing one correction method may disable another method.

4.4. Using further functionalities of *CarbX*

Once the measurement data are successfully fitted, other functions of the *CarbX* program can be used. Besides the possibility to export the current plot as an image and each curve as an X - Y file, the deviation between the data and the fit can be shown and exported in different ways. Furthermore, a list of all parameters given in Table 1 can be exported as a text file. The fit can also be stored as a template file for further usage.

4.5. Automatic fitting

To perform automatic fitting, the path to the *Mathematica* kernel has to be stored properly using the dialogue to set the program options. The automatic fitting is controlled entirely in

¹ *CarbX* supports both linear and decadic logarithm representation of the intensity. The scattering angle can be given either as $2\theta / ^\circ$ or already converted to the modulus of the scattering vector s . For the latter, the units nm^{-1} and \AA^{-1} are supported.

² In general, slider structures and input fields that are required for any chosen correction method are enabled, and additionally any slider structures for fit parameters that are always used are enabled at all times.

Table 2

Overview of the parameters of the CTP-800 sample obtained from the original publications and exported by *CarbX* after the respective verification step.

The parameters exported by *CarbX* were rounded to the same number of digits as the values given in the original publications. Values not listed here are not given in the corresponding original publication either. The errors of the parameters were estimated by monitoring the influence of changing the respective parameter on the fit quality as described by Faber *et al.* (2014b). Likewise κ_a was fixed to 0.25, *i.e.* $\nu = 1/\kappa_a$ was fixed to 4. As a result, κ_r was also set to a fixed value.

Parameter (symbol)	CTP-800 (Faber <i>et al.</i> , 2014b)	CTP-800 (typed in <i>CarbX</i>)	CTP-800 (fitted manually)	CTP-800 (fitted automatically)
L_a (Å)	19 ± 2.4	19 ± 2.4	20 ± 4.0	19 ± 2.4
$\langle l \rangle$ (Å)	16 ± 2.0	16 ± 2.0	16 ± 3.2	15 ± 1.9
κ_a	0.25	0.25	0.25	0.25
$\langle N \rangle$	2.0 ± 0.25	2.0 ± 0.25	2.0 ± 0.4	2.2 ± 0.28
N^*	3.9 ± 0.49	3.9 ± 0.49	3.7 ± 0.74	3.8 ± 0.48
L_c (Å)	13 ± 1.6	13 ± 1.6	13 ± 2.6	13 ± 1.6
κ_c	0.96 ± 0.12	0.96 ± 0.12	0.83 ± 0.17	0.76 ± 0.10
a_3 (Å)	3.44 ± 0.052	3.44 ± 0.052	3.44 ± 0.083	3.44 ± 0.052
σ_3 (Å)	0.26 ± 0.026	0.26 ± 0.026	0.24 ± 0.038	0.23 ± 0.023
ε_3	–	0.15 ± 0.023	0.11 ± 0.026	0.11 ± 0.017
κ_r	–	0.16	0.16	0.16

CarbX. Thus, it is not required to call *Mathematica* manually. A sufficient match between the data and manual prefitting is required before starting the automatic fitting as the problem is highly nonlinear. Further details can be found in §§3.3 and 2.3.3 of the supporting information.

4.6. Further information

Fig. 9 shows a schematic flow chart of steps required to fit WAXS data of NGCs. The dialogue to choose a template as well as the automatic fitting using *Mathematica* is optional.

For verification purposes, *CarbX* is equipped with the data file `HEP_RT.xy` and its corresponding NGC file `HEP_RT.ngc`. These files can be used to verify the correct functioning of *CarbX*, including the automatic fitting if *Mathematica* is available.

The steps required in three typical applications of *CarbX* are described in the supporting information.

The source code of the program, excluding the *Numerical Recipes in C* and WSTP source files, can be downloaded from <https://www.uni-giessen.de/CarbX-source>.

5. Application of the *CarbX* program

For verification purposes, the program *CarbX* was tested to reproduce fits of WAXS of the carbonized coal tar pitch (CTP-800), activated carbon (AC Type H) and carbonized furfuryl alcohol (FA-850) samples described by Faber *et al.* (2014b), as well as the poly(ionic liquid) carbon fibre (PIL) sample described by Einert *et al.* (2015). First, the parameters given in these articles were manually typed into *CarbX*. Second, the WAXS data of the samples listed above were fitted manually in *CarbX*. When available, a suitable template was chosen for

Table 3

Overview of the parameters of CTP-800, AC Type H, PIL and FA-850 obtained by automatic fitting in *CarbX*.

The parameters exported by *CarbX* after the final automatic fitting step were rounded to the same number of digits as the values given in the original publications. Values not listed here are not given in the corresponding original publication either. The errors of the parameters were estimated by monitoring the influence of changing the respective parameter to the fit quality as described by Faber *et al.* (2014b). Likewise κ_a was fixed to 0.25, *i.e.* $\nu = 1/\kappa_a$ was fixed to 4. As a result, κ_r was also set to a fixed value.

Parameter (symbol)	CTP-800 (Faber <i>et al.</i> , 2014b)	CTP-800 (<i>CarbX</i>)	AC Type H (Faber <i>et al.</i> , 2014b)	AC Type H (<i>CarbX</i>)
L_a (Å)	19 ± 2.4	19 ± 2.4	32 ± 4.0	31 ± 3.9
$\langle l \rangle$ (Å)	16 ± 2.0	15 ± 1.9	26 ± 3.3	24 ± 3.0
κ_a	0.25	0.25	0.25	0.25
$\langle N \rangle$	2.0 ± 0.25	2.2 ± 0.28	1.8 ± 0.23	1.8 ± 0.23
N^*	3.9 ± 0.49	3.8 ± 0.48	2.1 ± 0.27	2.0 ± 0.25
L_c (Å)	13 ± 1.6	13 ± 1.6	7 ± 0.88	7 ± 0.88
κ_c	0.96 ± 0.12	0.76 ± 0.10	0.15 ± 0.019	0.12 ± 0.015
a_3 (Å)	3.44 ± 0.052	3.44 ± 0.052	3.60 ± 0.054	3.56 ± 0.053
σ_3 (Å)	0.26 ± 0.026	0.23 ± 0.023	0.57 ± 0.057	0.50 ± 0.050
ε_3	–	0.11 ± 0.017	–	0.19 ± 0.029
κ_r	–	0.16	–	0.16

Parameter (symbol)	PIL (Einert <i>et al.</i> , 2015)	PIL (<i>CarbX</i>)	FA-850 (Faber <i>et al.</i> , 2014b)	FA-850 (<i>CarbX</i>)
L_a (Å)	20 ± 2.5	20 ± 2.5	25 ± 3.1	23 ± 2.9
$\langle l \rangle$ (Å)	–	16 ± 2.0	20 ± 2.5	19 ± 2.4
κ_a	–	0.25	0.25	0.25
$\langle N \rangle$	1.7 ± 0.21	1.7 ± 0.21	1.5 ± 0.19	1.6 ± 0.20
N^*	–	3.0 ± 0.38	2.3 ± 0.29	2.3 ± 0.29
L_c (Å)	11 ± 1.4	11 ± 1.4	8 ± 1.0	8 ± 1.0
κ_c	0.77 ± 0.096	0.77 ± 0.096	0.51 ± 0.064	0.42 ± 0.053
a_3 (Å)	3.63 ± 0.054	3.64 ± 0.055	3.60 ± 0.054	3.61 ± 0.054
σ_3 (Å)	0.54 ± 0.054	0.56 ± 0.056	0.43 ± 0.043	0.44 ± 0.044
ε_3	–	0.21 ± 0.032	–	0.20 ± 0.030
κ_r	–	0.16	–	0.16

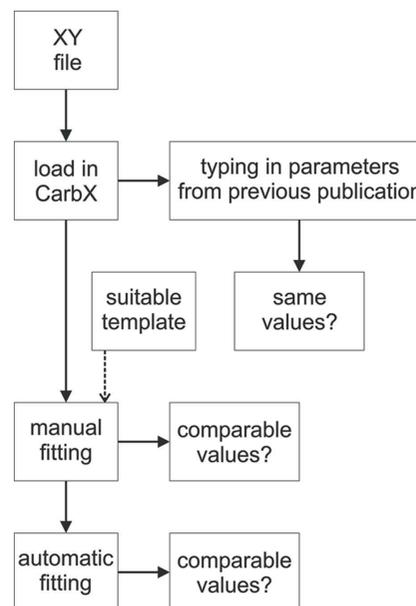


Figure 10

Flowchart of the process used to verify the *CarbX* program. All steps were performed for each sample shown in this publication. In each case, comparable values, *i.e.* values that coincide within their respective error margins, were obtained.

each sample. The parameters obtained by this manual fitting served as good initial values for the subsequent automatic fitting procedure. Automatic fitting using *Mathematica* as described in §§3.3 and 2.3.3 of the supporting information was performed using the default sequence supplied in the ZIP archive of the *CarbX* program. Fig. 10 depicts this verification scheme. Table 2 lists the reference values of the CTP-800 sample parameters given in the previous publication together with those obtained by copying the parameters into *CarbX*, those obtained by manual fitting and those obtained by

automatic fitting. The parameters calculated by *CarbX* after copying in the parameters given in the previous publication have the same value, if rounded accordingly, as the parameters given in the reference. For all samples the parameters given in the original publication together with those obtained by automatic fitting are listed in Table 3. All parameters, except those given in the previous publications, were taken from the list exported by *CarbX*. The parameters obtained by automatic fitting are in good agreement with the parameters given in the previous publications. The deviations result from both slightly

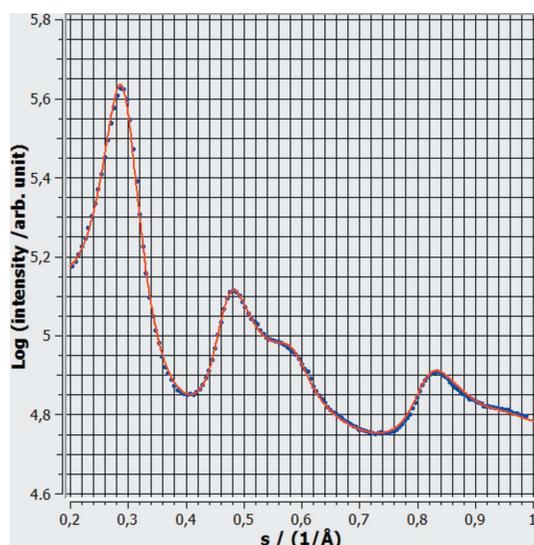


Figure 11
Fit (red solid line) of the WAXS data (blue dots) of coal tar pitch carbonized at 800°C (1073 K) created with *CarbX*. Here the results of the automatic fitting are depicted. As the fit shows no significant deviation, *CarbX* was successfully used for this fit.

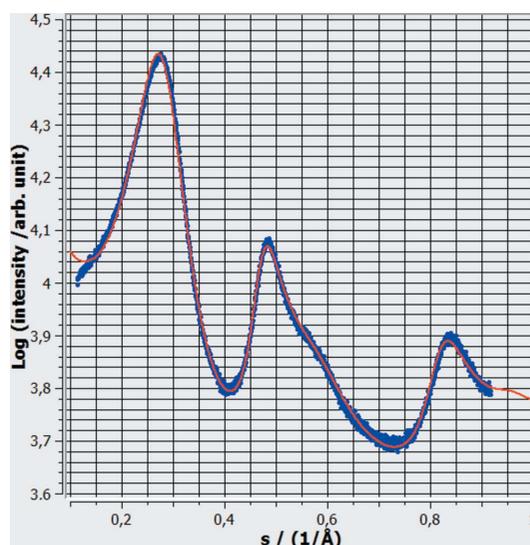


Figure 13
Fit (red solid line) of the WAXS data (blue dots) of a poly(ionic liquid) carbon fibre created with *CarbX*. Here the results of the automatic fitting are depicted. As the fit shows no significant deviation, *CarbX* was successfully used for this fit.

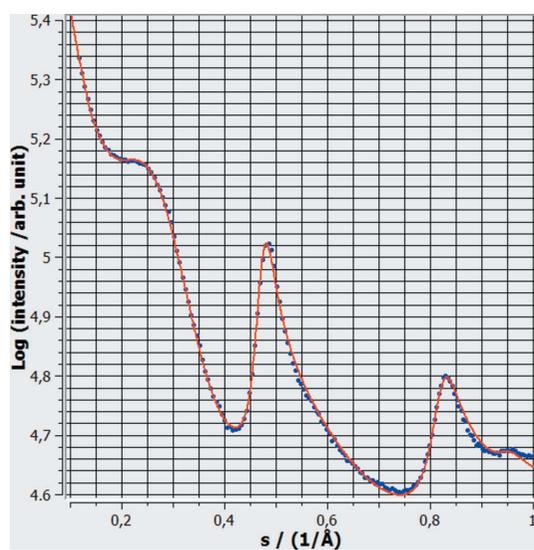


Figure 12
Fit (red solid line) of the WAXS data (blue dots) of activated carbon type H created with *CarbX*. Here the results of the automatic fitting are depicted. As the fit shows no significant deviation, *CarbX* was successfully used for this fit.

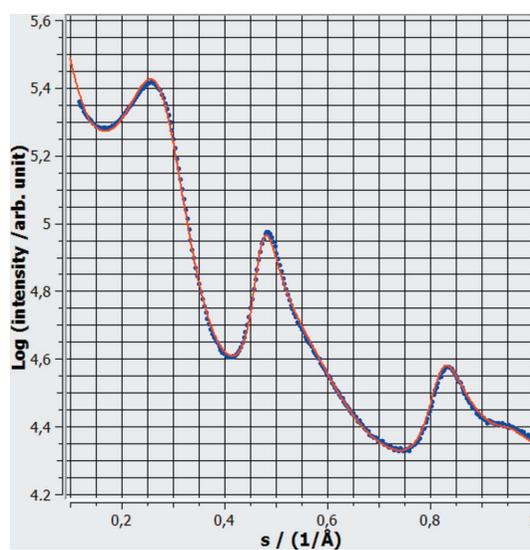


Figure 14
Fit (red solid line) of the WAXS data (blue dots) of furfuryl alcohol carbonized 850°C (1123 K) (FA-850) created with *CarbX*. Here the results of the automatic fitting are depicted. As the fit shows no significant deviation, *CarbX* was successfully used for this fit.

different initial values for the fit and a slightly different fitting sequence. The resulting plots, displaying good fits, are shown in Figs 11–14. The successful fit of the AC Type H sample proves the applicability of *CarbX* for highly disordered carbons. The samples were only measured for θ values from about 5 to 50° or 2θ values from about 10 to 100°, respectively, as this is the range typically used in laboratory setups.

6. Conclusion

With *CarbX*, a novel user-friendly program for a facilitated characterization of NGCs based on wide-angle X-ray scattering has been developed. To the best of our knowledge it is the first program available free of charge in this field, with the majority of its source code also published. In addition, a convenient GUI, hiding the complicated mathematics required, and *CarbX*'s unique features allow for easy analysis of the microstructure of non-graphitic carbons. Of particular note is *CarbX*'s template functionality by which non-experts are provided with reliable initial values, simplifying the task of fitting their measurement data. The usability of *CarbX* has been proven by verifying the underlying routines and by reproducing several fits shown in earlier publications. Further steps to be taken are to implement an inbuilt and independent algorithm for the automatic fitting to eliminate the need to use Wolfram *Mathematica* for this purpose. Moreover, support for

neutron scattering as well as for materials consisting of two phases of NGCs will be implemented in future.

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References

- Adelhelm, P., Cabrera, K. & Smarsly, B. M. (2012). *Sci. Technol. Adv. Mater.* **13**, 015010.
- Einert, M., Wessel, C., Badaczewski, F., Leichtweiß, T., Eufinger, C., Janek, J., Yuan, J., Antonietti, M. & Smarsly, B. M. (2015). *Macromol. Chem. Phys.* **216**, 1930–1944.
- Faber, K., Badaczewski, F., Oschatz, M., Mondin, G., Nickel, W., Kaskel, S. & Smarsly, B. M. (2014a). *J. Phys. Chem. C*, **118**, 15705–15715.
- Faber, K., Badaczewski, F., Ruland, W. & Smarsly, B. M. (2014b). *Z. Anorg. Allg. Chem.* **640**, 3107–3117.
- Fitzner, E., Kochling, K.-H., Boehm, H. P. & Marsh, H. (1995). *Pure Appl. Chem.* **67**, 473–506.
- Press, W. H., Teukolsky, S. A., Vetterling, W. T. & Flannery, B. P. (2000). *Numerical Recipes in C – The Art of Scientific Computing*, pp. 271–273. Press Syndicate of the University of Cambridge.
- Ruland, W. (1961). *Acta Cryst.* **14**, 1180–1185.
- Ruland, W. (1964). *Br. J. Appl. Phys.* **15**, 1301–1307.
- Ruland, W. & Smarsly, B. (2002). *J. Appl. Cryst.* **35**, 624–633.
- Shi, H., Reimers, J. N. & Dahn, J. R. (1993). *J. Appl. Cryst.* **26**, 827–836.
- Zickler, G. A., Smarsly, B., Gierlinger, N., Peterlik, H. & Paris, O. (2006). *Carbon*, **44**, 3239–3246.