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Automated Rotating TEM Simulations of Graphitic Material#

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ABSTRACT

The simulation of TEM images is computationally difficult. However, in the limit of completely amorphous materials, it can be simplified to the mass-thickness contrast only, neglecting any diffraction. Our method allows fast creation of TEM images of char models and allows to find an optimal viewing angle. The intention of our char models is to investigate the stacking and bending of graphitic carbon systems. To count the planes of a stack and determine the plane length and curvature one needs specific angles to create the TEM image. A good angle gives a high contrast between carbon layers. In this paper, we show TEM simulations of four different carbon structures.

Keywords: mass-thickness contrast, electron tomography, hydrogen, carbon

NOMENCLATURE

Abbreviations	
TEM	Transmission Electron Microscopy
EDIP	Environment-dependent interaction potential
GAP	Gaussian approximation potential
ReaxFF	Reactive force field
VMD	Visual molecular dynamics

1. INTRODUCTION

TEM imaging is an essential tool to investigate the structure of char. With the electron beam, one can generate a magnified image on an atomistic scale. In TEM images of char samples, one can see the stacking of the planes and the image can be analyzed to determine the stacking height, plane length, and the curvature of the sample [1].

The experimental information is pivotal to simulate good char models. The incorporation of experimental (HR)TEM results when creating coal or char models is common [2]. The way of including the experimental results, however, differs. Several studies use a single 2D TEM image as experimental input and use different extrapolations to generate a 3D carbon model [3-5].

Currently, we are working on a novel method for the preparation of char models, where the size and curvature of the graphitic planes can be taken as input [6]. The simulation of a TEM image from that model brings us full circle regarding the experimental input data (Fig. 1). On the long run, the model creation and TEM image simulation will become an iterative step to reproduce experimental data. A fringe analysis of HRTEM images [1] is a promising tool to acquire experimental information on carbon material and later compare that with the simulated TEM image.

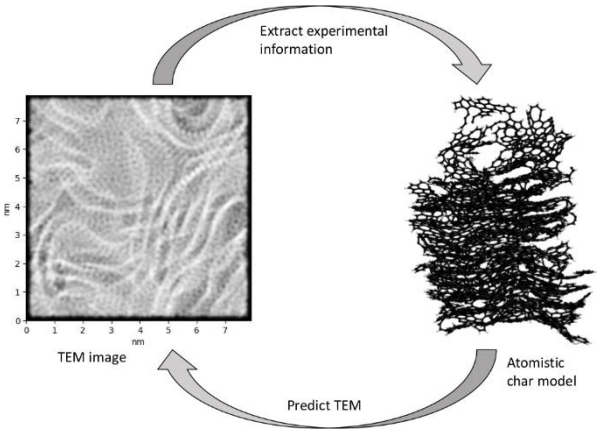

Fig. 1 Full circle TEM-model

The TEM simulation of sending electrons through matter is complicated and various techniques and codes create TEM images with varying methods, giving different information on the sample [7-9]. The TEM image simulation has two parts. The first is the mass-thickness contrast or electron tomography, where the ratio of electrons that passes through the sample is determined. The more involved aspect is the diffraction of the electron beam within crystalline structures. There are several high-end TEM simulation methods that provide a grand range of possibilities to simulate the TEM image. This veritable cornucopia requires some skill and

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precise understanding, best from an experimental point of view for fruitful usage.

However, for amorphous carbon, we rely on an approach that has recently been proposed [10] for the simulation of TEM images with the mass-thickness contrast only. Based on the assumption, that diffraction is negligible, compared to mass-thickness contrast for a sample which is 100 % amorphous [10], like char, a substantially simpler, faster, and less complex simulation method can be applied. The method in Ref. [10] is lacking the inclusion of other atom types as hydrogen and oxygen atoms, which are the second and third most common atom types in char.

Our first objective is to simulate TEM images of char structures fast and simply by improving the previous method [10] for our system. Using the atomic number and the van der Waals radius for the model simulation, we expanded the method by many elements. In Ref. [10] the simulation is accelerated by not applying the Lambert-Beer law (Eq. 2), however, we found it helpful for an improved image of the TEM simulation and determined a generalized value for σ.

The second objective of this work is to find a systematic strategy to locate an optimal angle for visualization automatically. When simulating TEM images for char models, the resulting images differ of course depending on the angle at which the electron beam hits the sample. The relevant information we need is about the planes and the stacking, and an optimal angle needs to be identified to see that. Therefore, an automated workflow is needed to find the most promising views.

2. TEM SIMULATION

2.1 Method

The automated rotating TEM simulation approach consists of two components: The TEM simulation from only the mass-thickness contrast and a routine that determines the desired angles.

2.1.1 *Calculation of mass-thickness contrast*

Following the routine from Ref. [10], the char model is positioned over the 2-dimensional image plane which is distributed in bins. The number of bins varies with the size of model. We have used 5 bins/Å during the calculations and 15 bins/Å for the final image to accelerate the calculations and improve the image quality.

For every atom in the model with position x_0, y_0, we add within its van der Waals radius vdW a Gaussian modified value g to the bins. Z is the atomic number namely protons in the atom and used as multiplier [11].

$$g = Z * \exp\left(-\frac{(x-x_0)^2}{\frac{vdW}{2}} - \frac{(y-y_0)^2}{\frac{vdW}{2}}\right) \qquad 1$$

To calculate the transmission $\frac{\Delta I}{I}$ we apply the Lambert-Beer law to all bins. N is the sum of g per bin.

$$\frac{\Delta I}{I} = 1 - e^{-\sigma N} \qquad 2$$

As discussed in 2.2.1 we choose $\sigma = 2.5/N_{max}$ because that gives the TEM images with the best contrast.

2.1.2 *Angle*

The angle of the sample strongly influences the expressiveness of the TEM images. If one looks upon the top of a stack of carbon planes, one hardly gains information. We want to look onto a stack from the side to see the carbon planes. That means from the desired view, there are strong contrasts between the planes and the plane spacing. Translated in a TEM image that means we search for bins with a high atom count. We found to compare the sum of the 30 bins with the highest value of the simulated images gives a good comparison. We developed a routine that rotates the sample, simulates

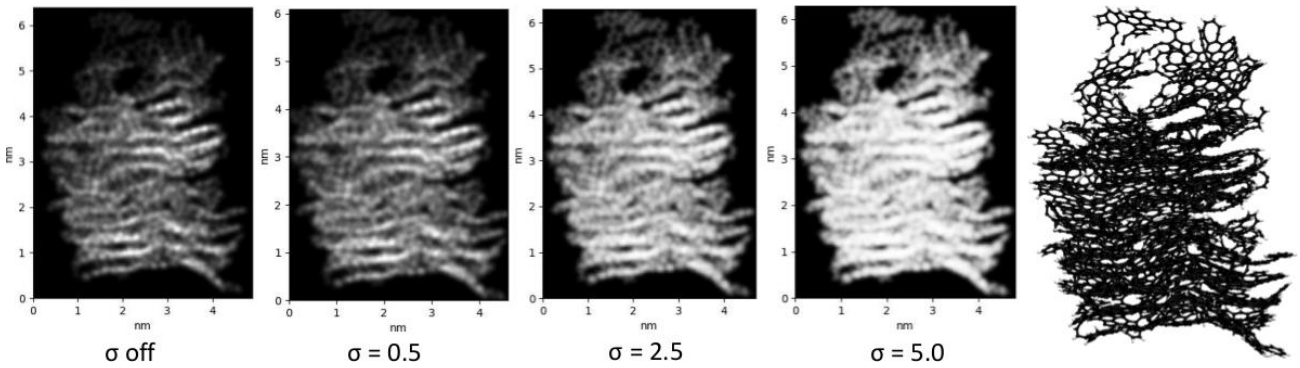

Fig. 1 Our 13 layer char model with the TEM images, in the leftmost image we did not apply the Lambert-Beer law, in the three other TEM images we chose σ-values as given*, on the right is an atomistic visualization of the same angle of the char model*

the TEM images, and compares them to find a good angle.

For the rotation of the model, we use Euler angles. The intention is to roughly check several angles from one side of the model. For this 0, 0.8 and 1.6 were chosen as first rotation values. A combination of the three rotation values for the three axis x, y, and z results in 27 angles to simulate an image from. The routine finds the best angle; here, however, a check is necessary as explained in the example in 2.2.1. The next step is identical, only using smaller angles: 0.2, 0.4, and 0.6 creating 27 images. This slightly rotates the sample in proximity of the initial image coming no further to the other simulated angles than necessary. As we have determined a good angle already, we only want some fine tuning in that region.

2.2 Results & Discussion

First, we computed TEM images for a char model prepared by our novel construction method, based on a stack of bend planes [3]. Here we have several stacked carbon planes saturated with hydrogen atoms. The model was created with ReaxFF [12-13]. We also used three models from Ref. [14-16] that appeared promising. These are boxes of 4-8 nm filled with carbon atoms.

We provide the atomistic image of the models made with VMD [17] and the TEM image in the same rotation next to each other. The depth of the TEM image is approximately the same as the length, if not stated differently.

2.2.1 Non-periodic char model

The char model has 4,873 atoms, a stack of 13 layers and plane lengths of less than 50 Å. In Ref. [10] it was stated that the relative intensity is proportional to the number of atoms in a specific histogram bin, which means one could skip the application of the Lambert-Beer law. This results in a reduced numerical effort per bin. We simulated one TEM image without applying the Lambert-Beer law and three with the Lambert-Beer law where σ equals 0.5, 2.5, and 5.0 (Fig. 2). Comparing the TEM simulation without Lambert-Beer law with the others, we see the general shape is obviously the same, with a difference is the contrast. The brightest bins in both TEM images have the same color. Due to the exponential part of the Lambert-Beer law, the planes appear much clearer, which is also contributed by the selection of the σ. We chose $\sigma\mathrm{N} \leq 2.5$, giving the best contrast for our images.

For comparison we show two more images of $\sigma\mathrm{N} \leq 0.5$ and $\sigma\mathrm{N} \leq 5.0$. If σ is bigger, the planes appear thicker, becoming hard to distinguish from each other. The atoms of the top plane are clearly visible, apparently even the bonds, however, for us it is more important to gain information about the stacks rather than visualizing every atom. If σ is smaller there is less contrast between the planes and the atoms from the top plane which clearly appear in the image with $\sigma\mathrm{N} \leq 5.0$ are nearly invisible. The image is very similar to the TEM simulation without Lambert-Beer law, though already more structures can be seen. $\sigma\mathrm{N} \leq 2.5$ is a good compromise between distinguishing the layers from one another and visualizing small atomistic structures like the top layer.

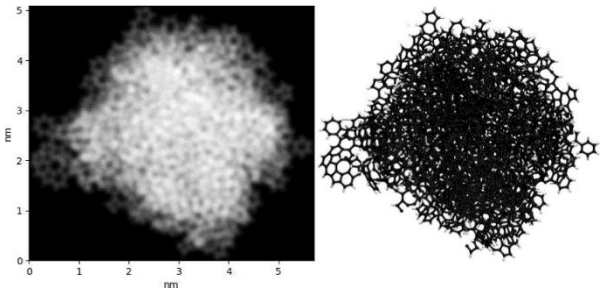

Fig. 2 Top view onto the 13 layer char model, the depth of the TEM image is approximately 6 nm

Our model has a stack of 13 layers and a plane length of maximal 50 Å. The image plane is distributed in a grid with bins, which count the partial carbon atoms above them. For a rough grid, most carbon atoms above one bin are likely, when looking from the top onto the stack (Fig. 3). When testing the grid factor and σ, in several runs, it was necessary to manually chose another angle and rerun the second angle comparison again.

To determine an optimal direction for the TEM image, the highest 30 Ns for every TEM image were summed up and compared. This is a fast and working approach, however, one of the next steps is to check and maybe improve this measure.

2.2.2 Periodic char models

Our models do not yet have the three-dimensional structure of real char. To proof that the method can be applied to large irregular structures, we used pure carbon models from Ref. [14-16] to produce TEM images. These models have been generated by placing exclusively carbon atoms in a simulation box and heating them with different reactive force fields above melting temperature to anneal the structure.

We chose models from three force fields. EDIP [18-19] is efficient for interatomic forces in covalent solids parametrized with ab initio data. GAP [20] is machine learned and parametrized with density functional tight binding and density functional theory. ReaxFF [12-13]

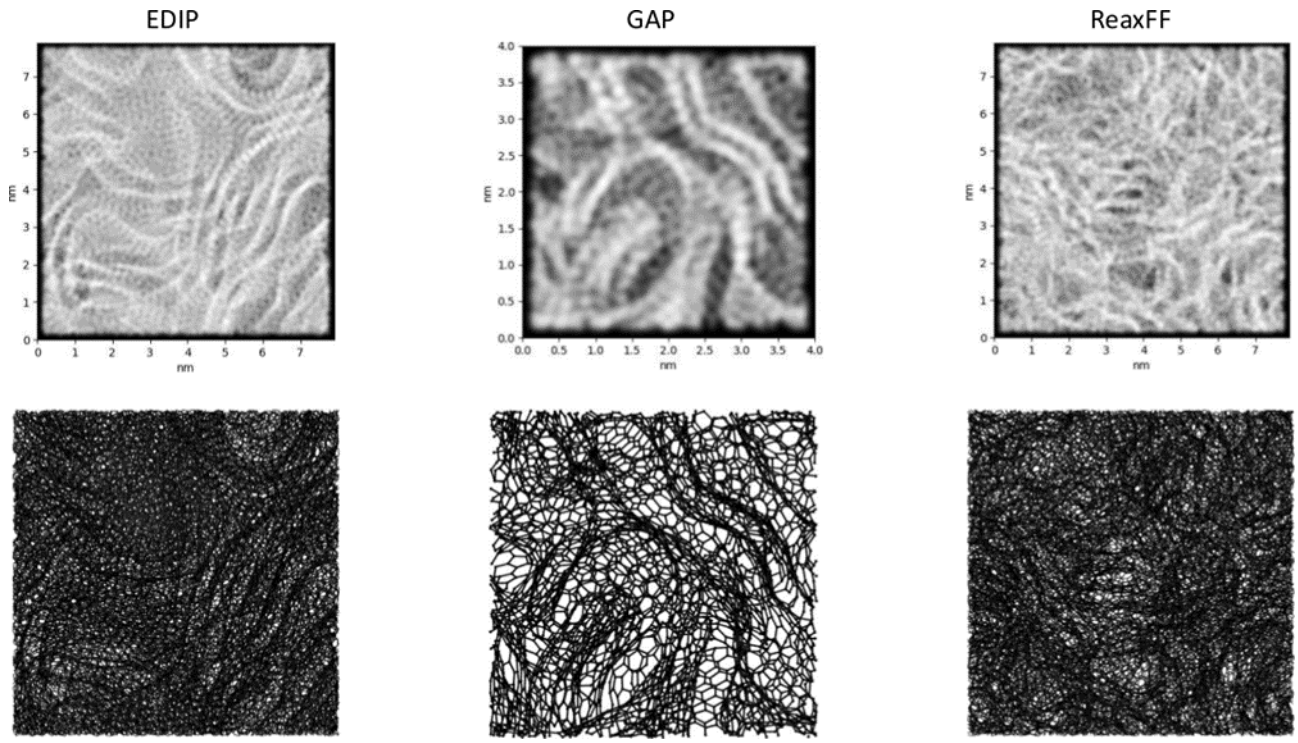

Fig. 3 TEM images of carbon models from carbonpotentals.org for the Force Fields EDIP, GAP, and ReaxFF of the angle with the biggest contrast, underneath the carbon model of the same view

parameters are derived from quantum chemical calculations.

Note, that these models have been generated with periodic boundary conditions. With the automated rotation approach, the optimal angle to be found for the truncated simulation boxes will result in a view direction onto an edge or even a corner. To avoid that, in this work only view directions onto the three sides of the cell in x, y and z direction were investigated. In the future one could use slab geometries cut from the periodic system along differently oriented planes to generalize the method for periodic systems.

EDIP: In the EDIP model are 32,768 carbon atoms. Here seems to be the biggest gain of information from model visualization to TEM image. In the model visualization we see some stacking, but mostly it is difficult to properly identify structures. In the TEM image however, we see a neat stacking of the layers in several areas which are also overlapping. So, we can even look in the structure and see more stacked planes than from the side we look at.

GAP: There are 4,096 atoms in the GAP model. They have formed aligned planes. We see many of the deeper structures from the model visualization. The TEM image simulation appears to be a proof rather than a mean to gain information.

ReaxFF: There are 32,768 atoms in the ReaxFF model. This makes an analysis from the outside difficult. Here however we do not see as much stacking as in the EDIP model. We see many single planes but and only few stacks, which do not align as neat as in the EDIP and GAP models.

The TEM image simulation works fine for carbon-hydrogen-systems. We plan to test other elements and we will check if the multiplier a being the number of protons is a good choice. So far, we suggest using no bigger atoms than chlorine, though that must be tested.

2.3 Conclusions

Most of the existing TEM simulation methods include the simulation of diffraction of the electron beam due to crystallinity of the sample. Their usage requires skill and at best experimental experience. We proposed a method to simplify the TEM simulations by assuming the sample is 100 % amorphous and neglecting diffraction. The calculation of the mass thickness contrast is fast, and we see good results for cells with a size of up to 8 nm in all three directions. We succeeded in automatizing the rotation of the sample to look onto the planes from the side. We applied the method to a small non-periodic char model and to periodic cells giving good results compared to the atomistic visualization.

In the TEM image of the EDIP potential we can even see the neat stacking of the layers, which is hard to see in the atomistic picture.

This tool will allow to compare atomistic char models with experimental char models easily. By combining this approach with the in-silico generation of char models

based on a predetermined curvature and size of the graphitic planes, a full simulation cycle will be possible in the future.

2.4 References

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