Model-based analysis of interface evolution during spray coating

Nikita Prudnikov

Moscow Institute of Physics and Technology, Moscow, Russia

Supervisor: Stephan V. Roth

September 3, 2021

Abstract

In this project, we aimed to simulate a GISAXS analysis of spray-coated organic thin films consisted of cellulose nanofibers with nanoparticles. The author of this report was supposed to model pure nanoparticles on the substrate to obtain scattering images similar to ones, which were get from the real experiment. Then, two parts of this project should have been joined and modified to repeat experimental results of the combined matter. This could have been helpful for nanofibers and nanoparticles thin films analysis in a simulated environment, without making real-life experiments to save synchrotron time and research resources. What could possibly go wrong?..

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Introduction

Spray coating plays a crucial role in modern organic thin film technology and is used for fabricating flexible electronics and photovoltaics. This technique was applied to create functional layers from materials science to biology. These structures and layers need to be thoroughly analyzed both in scales of a single layer and multilayer composition. Usually, surface-sensitive scattering methods are used for this analysis, where grazing-incidence scattering (GISAS) has an important place. One more way to research such structures is model-based computational analysis. The desired structure could be modeled in the real space, after that scattering pattern could be calculated via special software and compared to the experimental data. The goal of this project is to simulate such a structure: cellulose nanofibers with integrated nanoparticles, get a scattering image and compare it to the recently acquired experimental results. The project consists of two big parts: cellulose nanofibers (CNFs)[1] and nanoparticles (NPs),[2] which are supposed to be performed by different students and then combined.

This simulation is to be done using Bornagain software,[3] which is a free and open-source framework for simulating and fitting X-ray and neutron reflectometry and grazing-incidence scattering. This tool allows to simulate almost any possible structure and makes it possible to set a wide range of parameters to reproduce real-life experiment conditions.

Experiment

First, we must create a real-space model of nanoparticles on the substrate. We chose colloidal nanoparticles having a hydrophilic shell based on polymerized N,N-dimethylaminoethyl methacrylate (DMAEMA) and a hydrophobic core composed of PMMA. All the parameters were taken from the recent publication. [2]

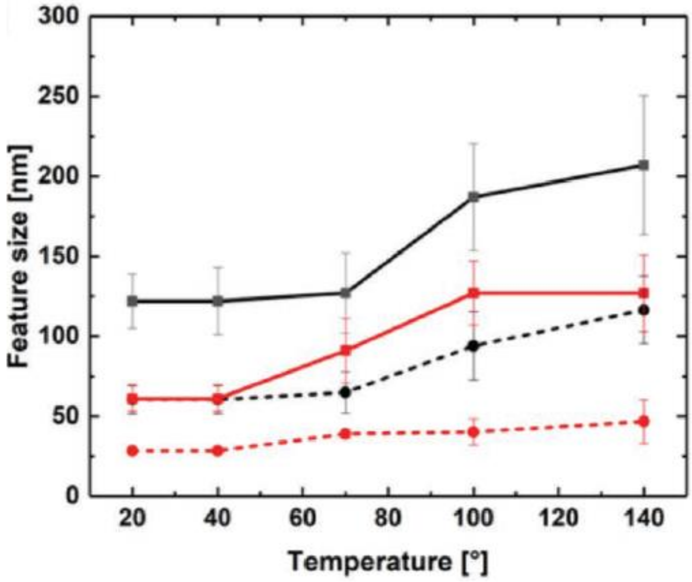

Figure 1. Size and distance between units of two types of domains [2]

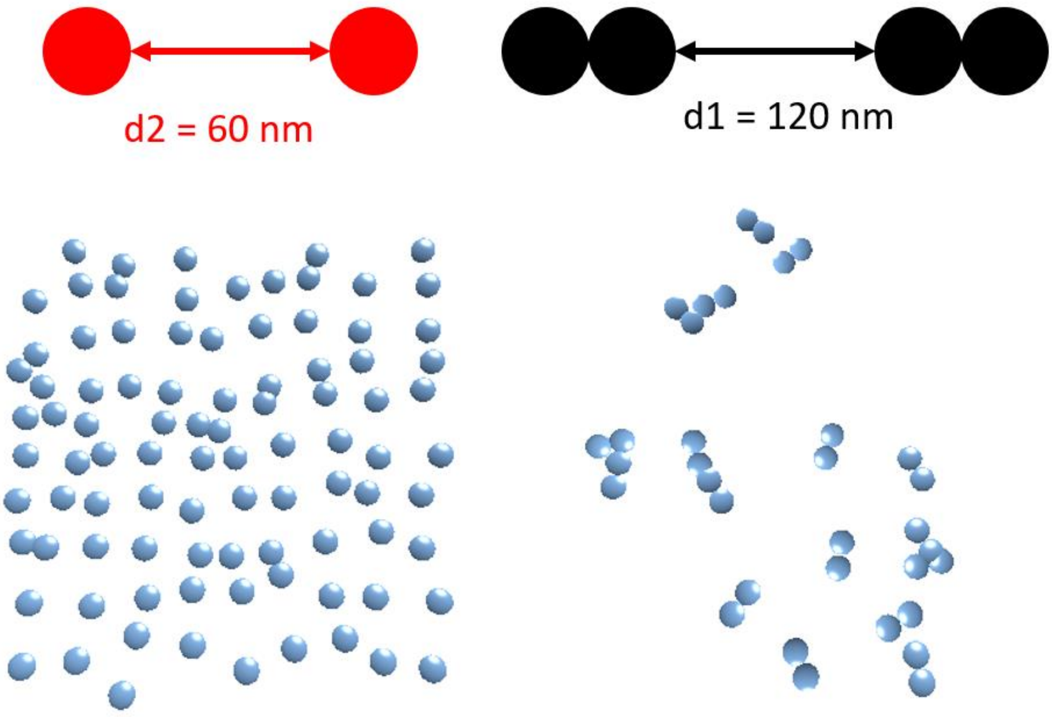

Figure 2. Distributions of two domains, used in the model

According to **Figure 1,** there are two types of domains in the structure. The first one was distinct particles of a radius approximately 30 nm (red dash line) and a distance of 60 nm between them (red solid line). The second one was a composition of particles with a radius of 60 nm (2 particles) and a 120 nm distance between them. These domains were modeled directly: in our model, we have set distinct particles and composition of two stuck particles randomly rotated around Z-axis. **Figure 2** shows the scheme of the two domains and their distribution on the substrate, after applying the same parameters as in the experiment.

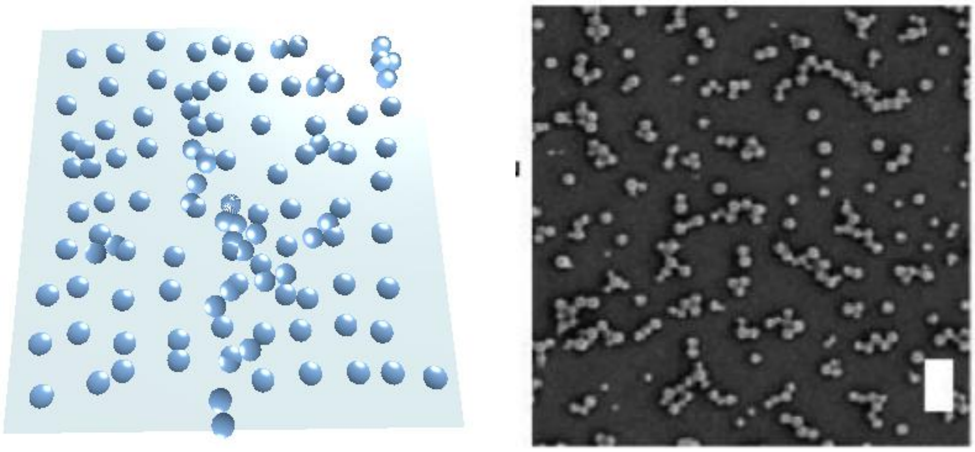

Figure 3. Model-based particle distribution (left) and real AFM image (right)

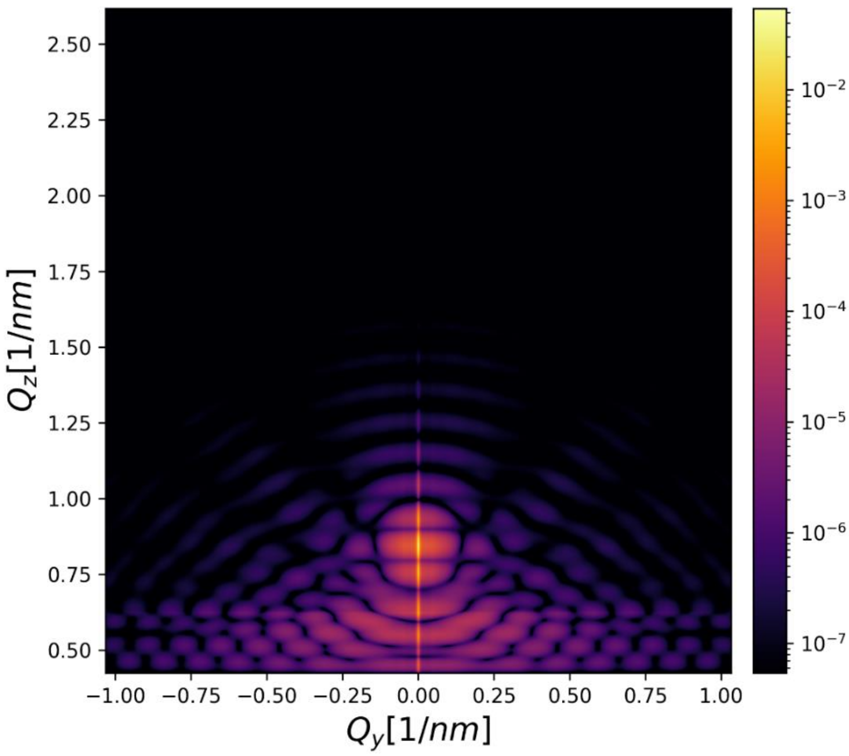

Figure 4. The scattering image obtained after lattice parameters search

Figure 3 (left) demonstrates a distribution of nanoparticles with two domains are combined on the substrate. Whereas the right image in **Figure 3** shows the real particle layer, obtained by atomic force microscopy (AFM). We have found these two pictures very similar and established that our model is accurate enough to simulate real particle distribution.

Moreover, particles were revealed to have a paracrystalline order. However, the parameters of the lattice are unknown and were found after a great number of simulated and analyzed modeling experiments. **Figure 4** shows the result after the parameter search.

Thereafter, we have considered that the polymer nanoparticles have a certain contact angle with the surface, and it does not equal 180°. This angle was reported to be 65°, and this value was applied to our model. **Figure 5** demonstrates the result we obtained after this model modification.

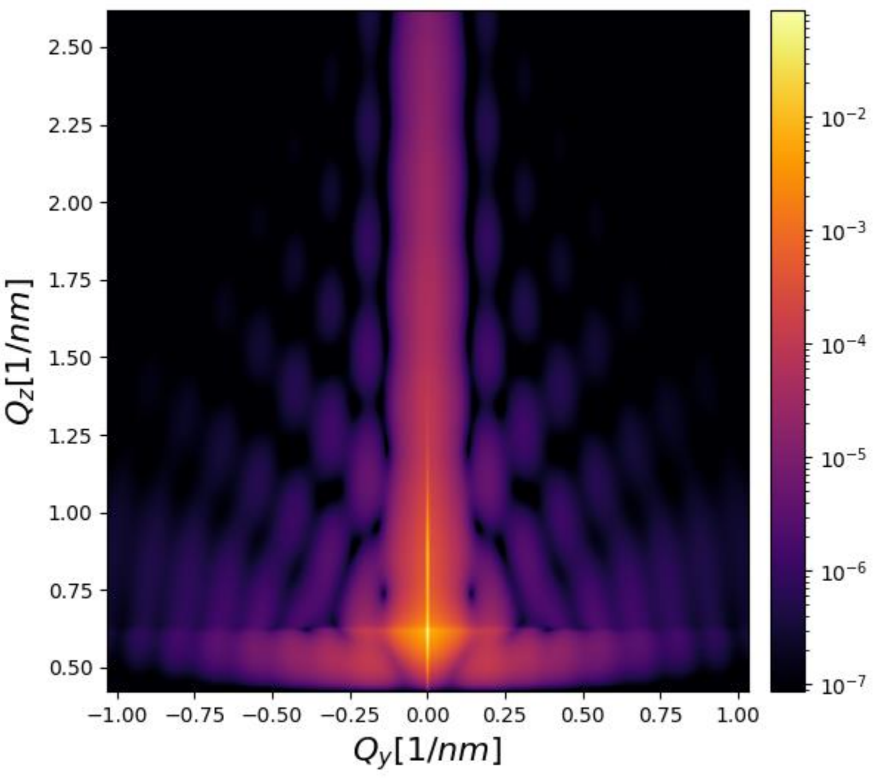

Figure 5. Scattering image after adding wettability and setting of contact angle

After taking into consideration the fact about contact angle we made the particles to be core-shell, as it was in the experiment. **Figure 6** shows the result obtained after the correction of this critical neglect. The target image, which was obtained during the real-life experiment is shown in **Figure 7**. It looks very similar: there is a strong central peak and there are also two side maximums, which are expected to be observed. However, our model still has the potential to be improved.

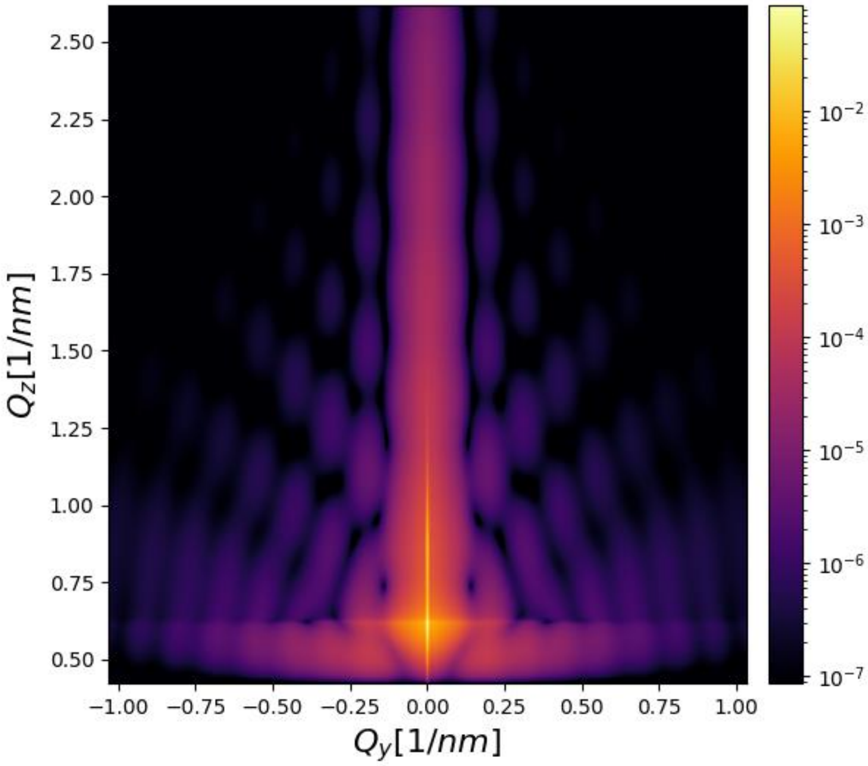

Figure 6. The final scattering image after turning particles into core-shell ones

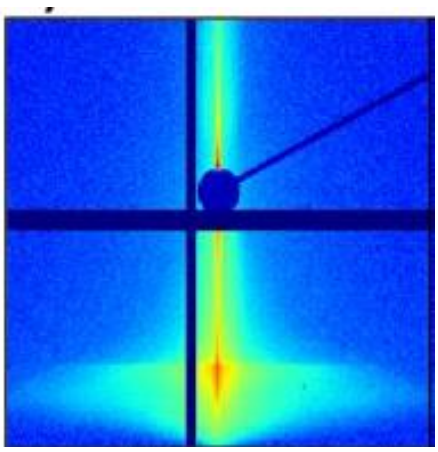

Figure 7. Target scattering image [2]

Conclusion

We have developed a real-space model of pure nanoparticles on a substrate and manually fitted the parameters of the lattice for scattering images to be similar to real experiment ones. We have improved our model having added a real contact angle value and turning our particles into core-shell ones. However, our model still has a lot of potential for improvement. An algorithm is needed to fit the parameters of the lattice in the software instead of manual adjustment. Moreover, the main goal of this project was to combine two parts made by different students to have a tool, which could provide scattering images of such a complex structure as CNFs with embedded nanoparticles. The success was so close, but our supervisor made an appointment and then missed the meeting. Then he repeated this combination once again. Following which he stopped replying to emails and we did not get any feedback from him. Nevertheless, we have got some results, have not we?

References

[1] C. J. Brett *et al.*, ‘Water-Induced Structural Rearrangements on the Nanoscale in Ultrathin Nanocellulose Films’, *Macromolecules*, vol. 52, no. 12, pp. 4721–4728, Jun. 2019, doi: 10.1021/acs.macromol.9b00531.

[2] J. Engström *et al.*, ‘Core–Shell Nanoparticle Interface and Wetting Properties’, *Adv. Funct. Mater.*, vol. 30, no. 15, p. 1907720, Apr. 2020, doi: 10.1002/adfm.201907720.

[3] G. Pospelov *et al.*, ‘*BornAgain* : software for simulating and fitting grazing-incidence small-angle scattering’, *J. Appl. Crystallogr.*, vol. 53, no. 1, pp. 262–276, Feb. 2020, doi: 10.1107/S1600576719016789.