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International Student Practice - Investigation and modeling of neutron/x-ray reflection by thin film of polymer nanocomposite-

Student

Danijela Rajić
Faculty of Technology,
University of Novi Sad, Serbia

Supervisor

Dr Timur Tropin
Frank Laboratory of Neutron Physics
JINR, Dubna, Russia

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Condensed-matter physics is the study of substances in their solid state. This includes the investigation of both crystalline solids in which the atoms are positioned on a repeating three-dimensional lattice, such as diamond, and amorphous materials in which atomic position is more irregular, like in glass.

Numerous nonequilibrium processes in condensed matter involve changes of atomic and electronic structure. The rearrangement of atoms in a phase transition or in a chemical reaction, charge relocations and changes of spin states in electron transfer and/or magnetic processes, as well as field-driven changes and mixing of electronic orbitals are among the most basic phenomena which determine functional properties.

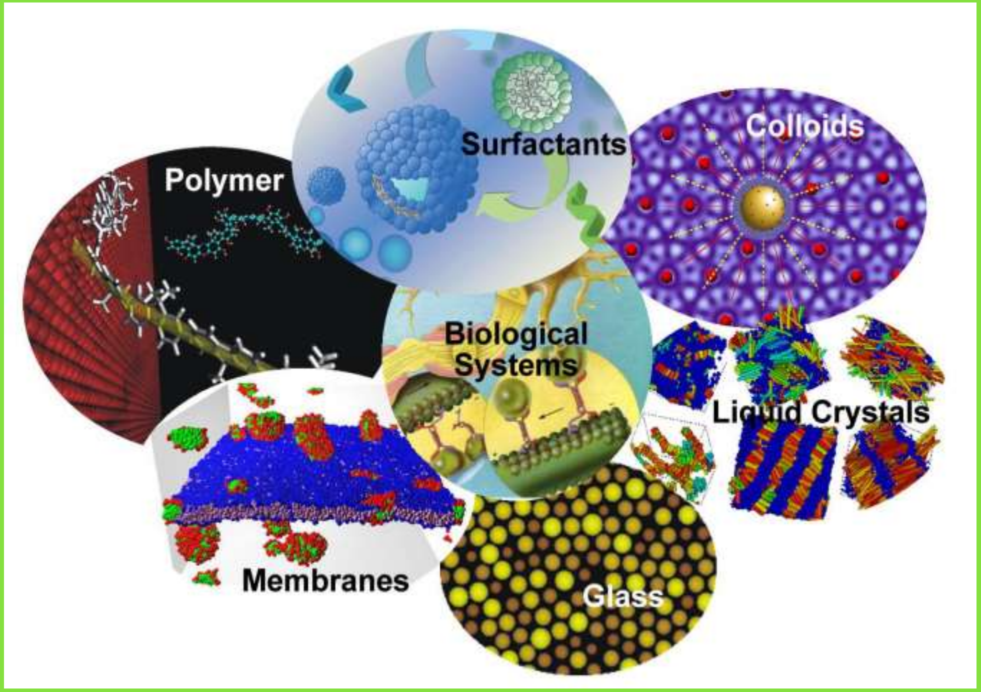

Figure 2. Structural research in condensed matter is an important tool for scientists

In the field of nanotechnology, one of the most popular areas for current research and development are polymer nanocomposites (PNCs) and the investigation field covers a broad range of topics. This would include nanoelectronics, polymeric bionanomaterials, reinforced PNCs, nanocomposite-based drug delivery systems, etc.

According to theoretical assumptions, idea of PNCs is based on the concept of creating a very large interface between the nanosized heterogeneities and macromolecules of neat polymer. The large interface between nanoparticles and macromolecules are supposed to result in unusual properties relative to conventional microfilled polymer composites.

In nanocomposites, large reinforcement and enhancing of other properties like decreased flammability and increased conductivityare often obtained at low concentration of nanofillers. However, those effects strongly depend on the homogeneous distribution of the nanoadditive in the polymer matrix that is hard to achieve.

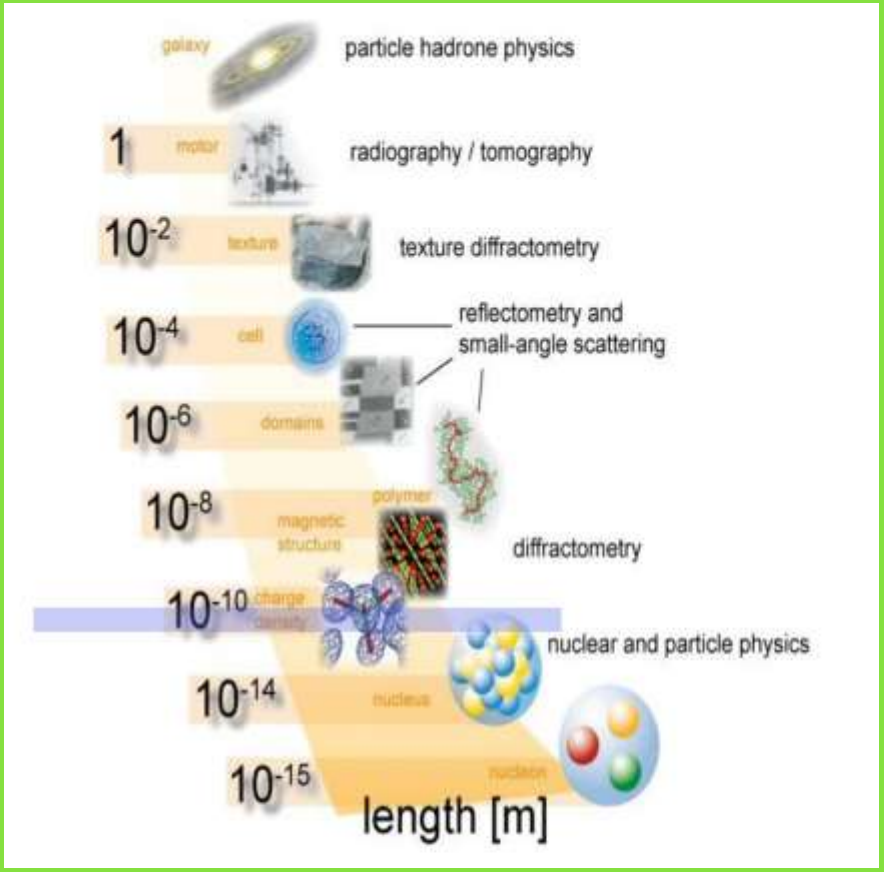

Figure 2. Characteristic length scales and corresponding research methods

Reflectometry uses the reflection of waves at surfaces and interfaces to detect or characterize objects.

There are many different forms of reflectometry.

They can be classified in several ways: **by the used radiation** (electromagnetic, ultrasound, particle beams), **by the geometry of wave propagation** (unguided versus wave guides or cables), **by the involved length scales** (wavelength and penetration depth versus size of the investigated object), **by the method of measurement** (continuous versus pulsed, polarization resolved, ...), and **by the application domain.**

Reflectometry is aimed at studying interfaces and thin film profiles.

Scattering techniques allow rapid, often real-time, noninvasive analysis of many types of materials in environments ranging from manufacturing plants to field-based measurements from aircraft. For this reason a large number of methods and applications have been developed.

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This course aims to determine the effect of the adding nanoparticles to thin films which change the the whole properties of the film.

These changes can be determined with neutron/x-ray reflectometry experiments. All curves, thin film modeling, and data fitting is done by Igor Pro software with Motofit package.

Some experimental data-Scattering wave vector $Q(A^{\circ -1})$ verses Reflectivity R- were extracted from reflectometry experiments, which contains backing and fronting media only and there is no existences for a thin films.

These experiments aim to obtain SLD value for the variable media -either backing or fronting- in order to determine the variable media. data from six experiments were extracted and fitted as a reflectivity curve using Igor Pro software with Motofit package.

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TASK 1

Air is the fronting media and an unknown liquid was used as the backing media. Reflectivity R values was recorded for 500 different value for scattering wave vector Q.

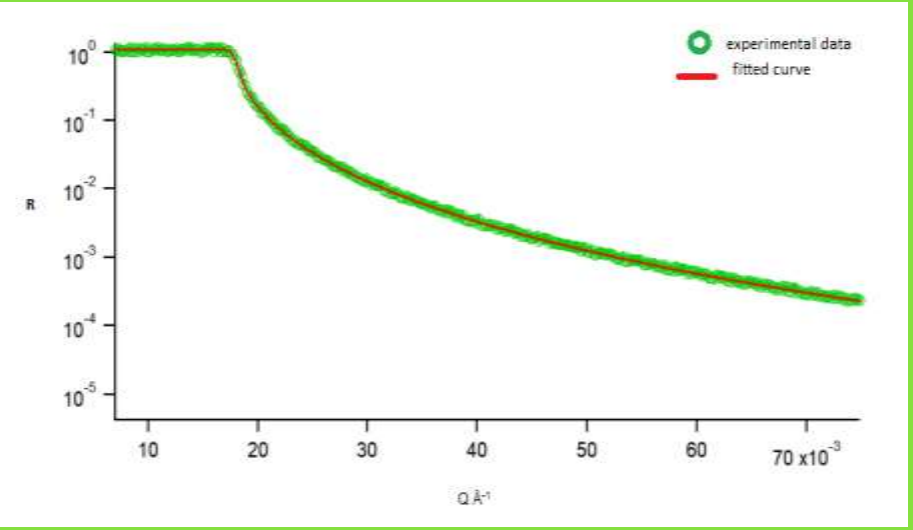

Figure 3. Reflectivity curve (unknown liquid)

The obtained value of SLD of backing media is $6.3352 \times 10^{10} cm^{-2}$, with $x^2 = 3.67 \times 10^{-4}$.

The SLD value show that the used liquid as backing media in this experiment is **D_2O**

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TASK 2

Air is a fronting media and an unknown solid was used as the backing media. Reflectivity R values was recorded for 500 different value for scattering wave vector Q.

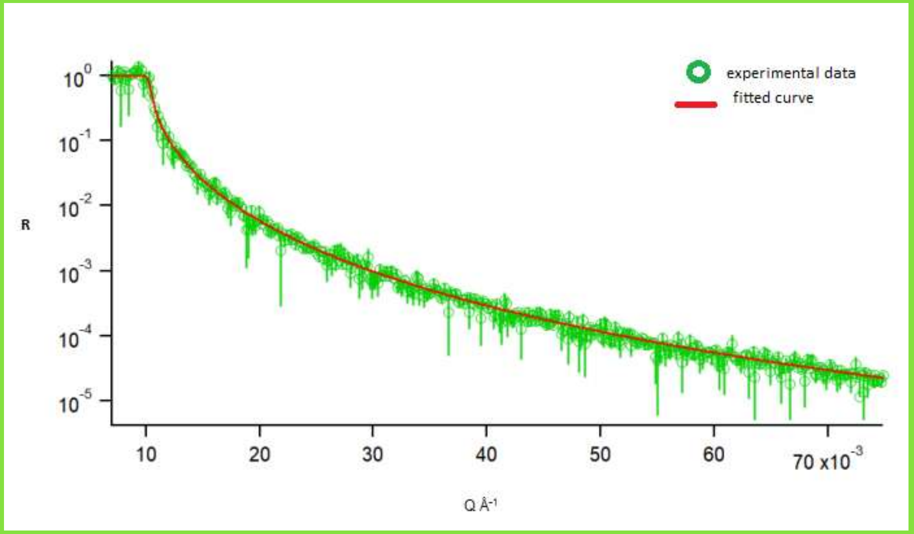

Figure 4. Reflectivity curve (unknown solid)

The obtained value of SLD of backing media is $2.0975 \times 10^{10} cm^{-2}$, with $x^2 = 1.735 \times 10^{-3}$.

The SLD value show that the used solid as backing media in this experiment is **Si.**

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TASK 3

The crystal is the backing media in task 2 is taken to be the backing media in this task, and an unknown liquid was poured on the crystal, to be used as the fronting media Reflectivity R values was recorded for 500 different value for scattering wave vector Q.

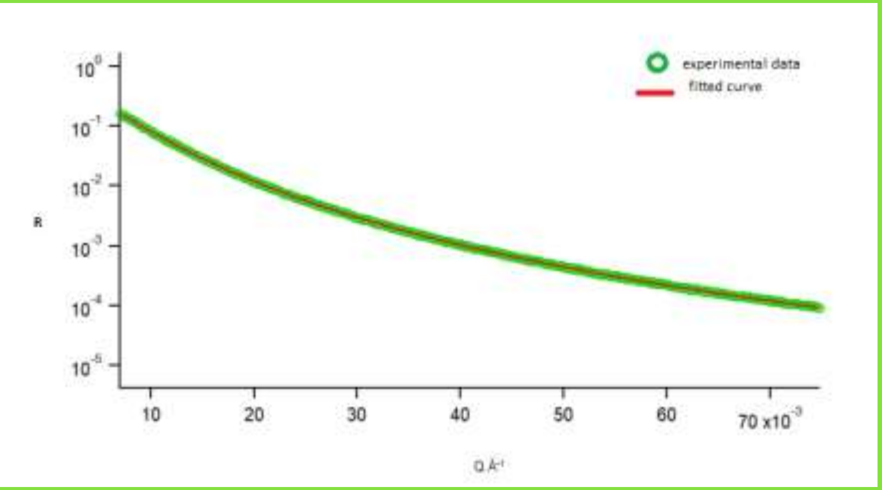

Figure 5: Reflectivity curve , with an unknown fronting media and Si crystal as backing

The obtained value of SLD of fronting media is $6.35 \times 10^{10} cm^{-2}$, with $x^2 = 3.35 \times 10^{-7}$.

The SLD value indicate that the used liquid as fronting media in this experiment is **D_2O.**

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TASK 4

An unknown crystal is the backing media, and D_2O was poured on the crystal to be used as fronting media. Reflectivity R values was recorded for 500 different value for scattering wave vector Q.

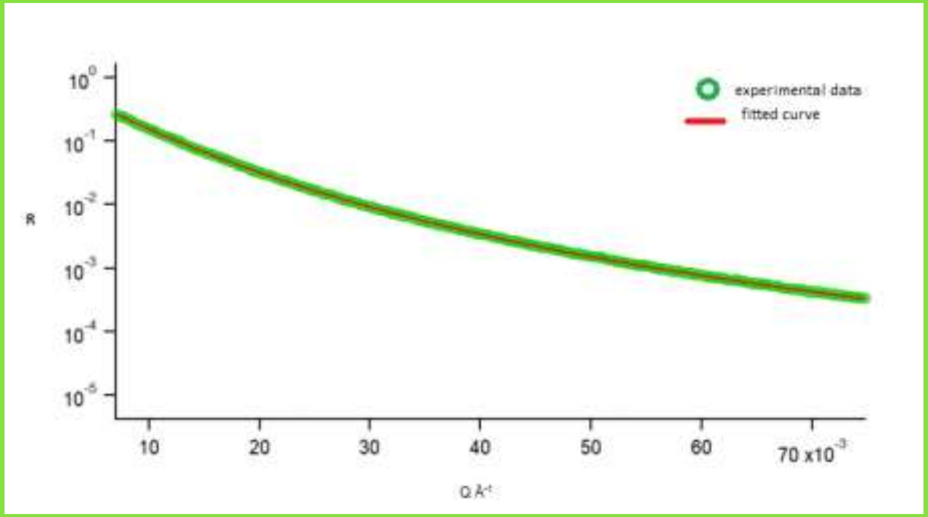

Figure 6. Reflectivity curve , with D_2O as fronting media and an unknown crystal as backing

The obtained value of SLD of fronting media is $-1.88 \times 10^{10}cm^{-2}$, with $x^2 = 1.169 \times 10^{-6}$.

The SLD value indicate that the used liquid as fronting media in this experiment is **Ti.**

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TASK 5

Anunknown liquid-that was used as the fronting media- was poured on Ni crystal that is used as a backing media. Reflectivity R values was recorded for 500 different value for scattering wave vector Q.

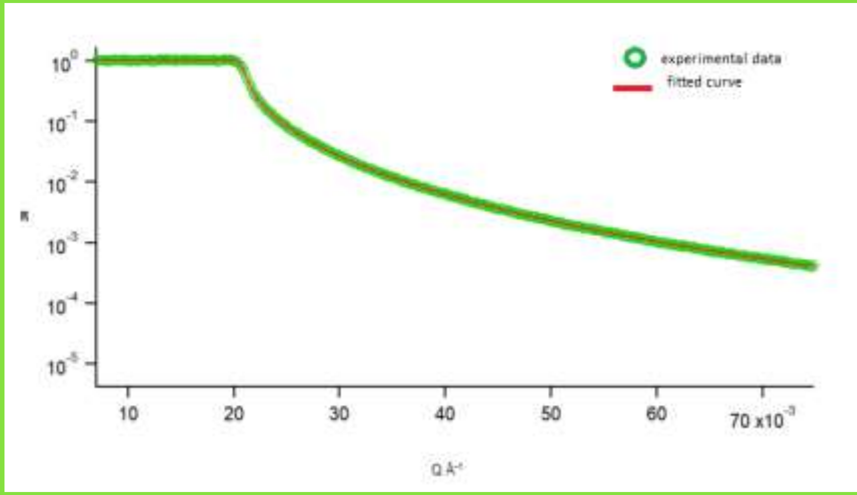

Figure 7. Reflectivity curve , with unknown liquid as fronting media and an Ni crystal as backing

The obtained value of SLD of fronting media is $0.94 \times 10^{10} cm^{-2}$, with $x^2 = 7.62 \times 10^{-5}$.

The SLD value indicate that the used liquid as fronting media in this experiment is organic compound **$C_6H_5CH_3$ (toluene).**

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TASK 6

An unknown liquid -that was used as the fronting media- was poured on Ni crystal that is used as a backing media. Reflectivity R values was recorded for 500 different value for scattering wave vector Q.

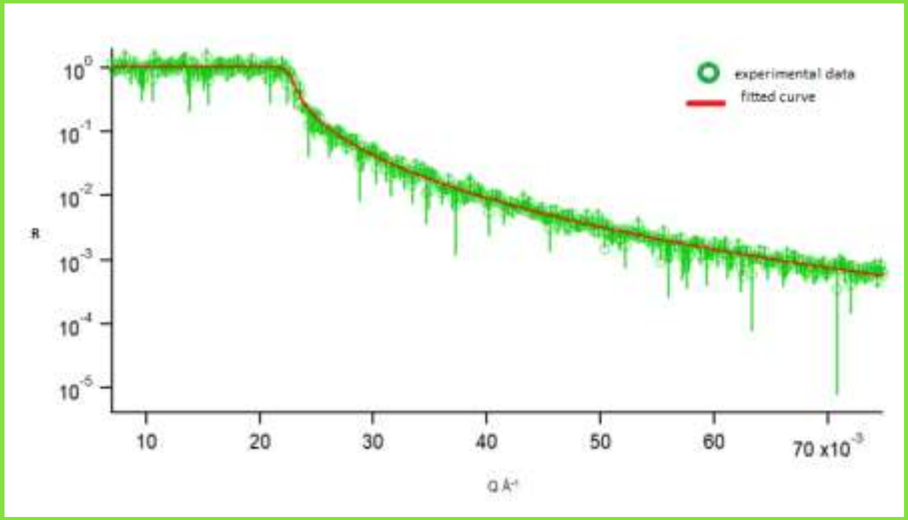

Figure 8. Reflectivity curve , with unknown liquid as fronting media and an Ni crystal as backing

The obtained value of SLD of fronting media is -0.56×10^{10}cm^{-2}, with $x^2 = 7.7 \times 10^{-3}$.

The SLD value indicate that the used liquid as fronting media in this experiment is **H_2O.**

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THIN FILM MODELLING (WITHOUT ROUGHNESS)

Different versions of 500 A˚ polystyrene thin films which are doped with 5% mass of fullerene NPs C60 are modeled. Every model is characterized by NPs1 distribution inside the film either uniform, or substrate and air with 100% NPs content in layer.

The reflectometry experiments are designed such that the fronting media is the air with $\rho_{film}=0$, and Si crystal as backing media with $\rho_{film} = 2.07 \times 10^{10}\ cm^{-2}$ and the film is inserted in between.

A reflectivity curve is generated for every case by generating 500 point in the range between $Q = 0.007A^{\circ -1}$ and $Q = 0.075A^{\circ -1}$, also SLD curves are generated for every case.

The polystyrene thin film has scattering length density $\rho P\ S = 1.35 \times 10^{10} cm^{-2}$. When the film doped with fullerene NPs, the SLD value changes according to the following relations:

- in the case of uniformly distributed NPs $\rho_{eff} = \rho_{film} + \phi(\rho NP\ s - \rho_{film})$
- in the case of dense layer (substrate and air) $\rho_{layer} = \rho film + \phi L(\rho NP\ s - \rho film)$.

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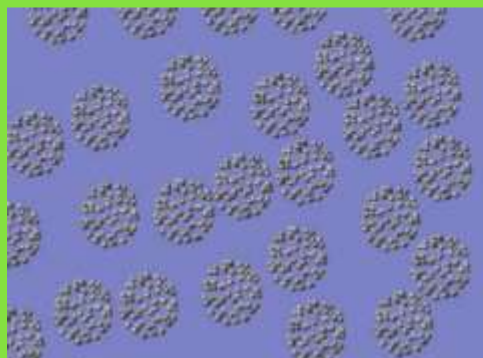
Uniformly Distributed NPs



A 500˚A polystyrene thin film that is doped with 5% mass of fullerene NPs which are distributed uniformly is designed. According to equation 1 the effective SLD value of the film is ρfilm = $1.569 \times 10^{10} cm^{-2}$.

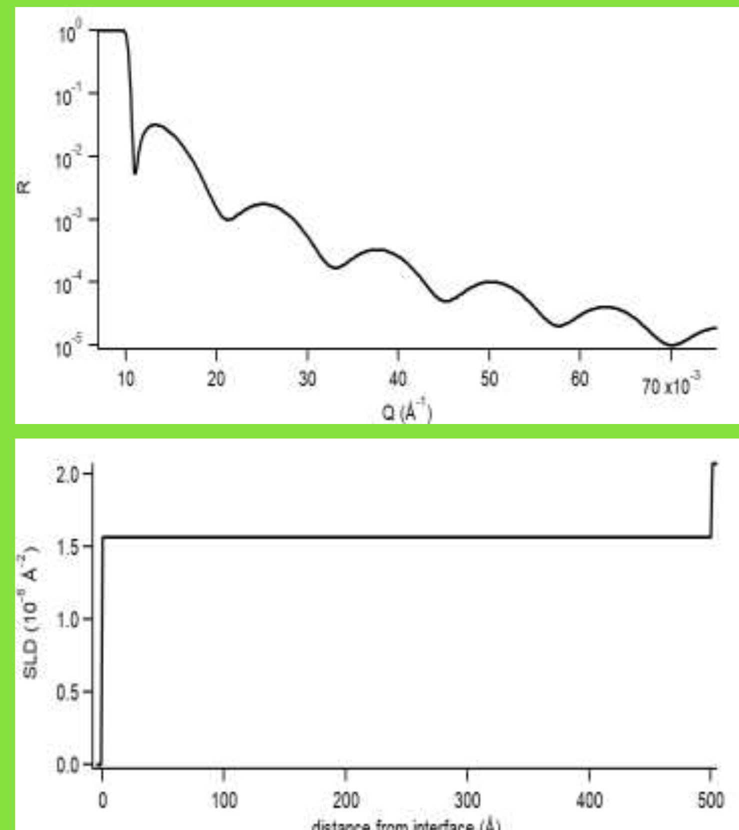


Figure 9. Reflectometry results of 500˚A polystyrene thin film, with uniformly distributed fullerene NPs a) reflectivity curve, b) SLD curve

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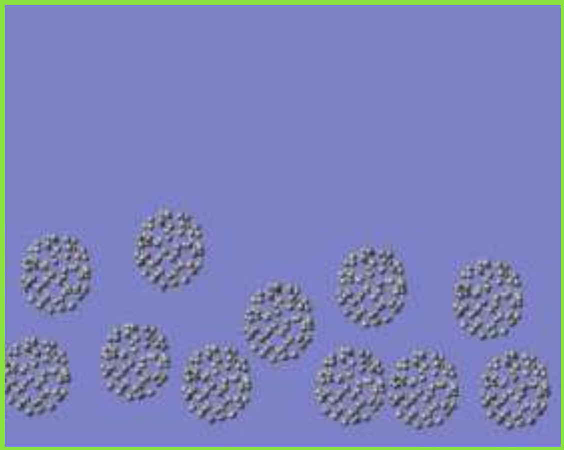
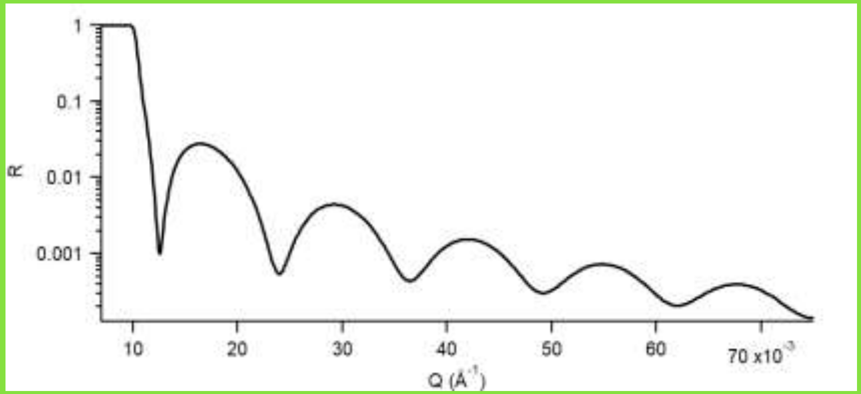
Substrate layer



A 500˚A polystyrene thin film that is doped with 5% mass of fullerene NPs which are combined to form a dense layer of fullerene with length δlayer = 25˚A, that is close to the backing media. As the content of NPs in the layer ϕL = 100%, according to equation 2 this layer has SLD value ρlayer = 5.73 × $10^{10}cm^{-2}$, then the film can be considered as two layers; the first one is polystyrene layer which has length δP S = 475˚A, and the second one is fullerene layer which has length δC60 = 25˚A.



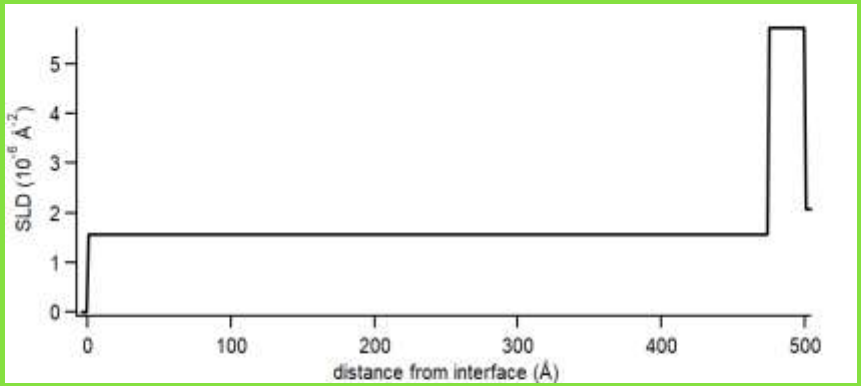


Figure 10. Reflectometry results of 500 ˚A polystyrene thin film, with substrate layer of fullerene NPs
a) Reflectivity curve, b) SLD curve

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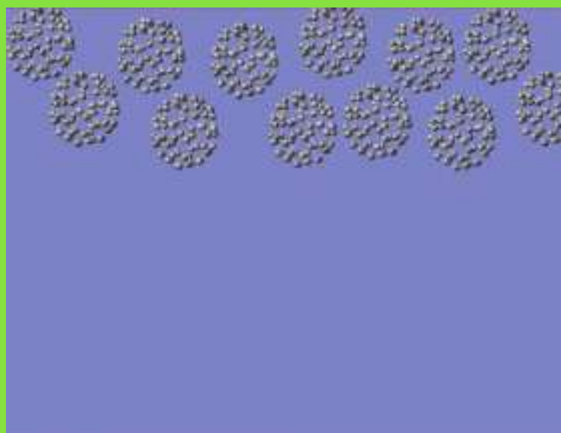
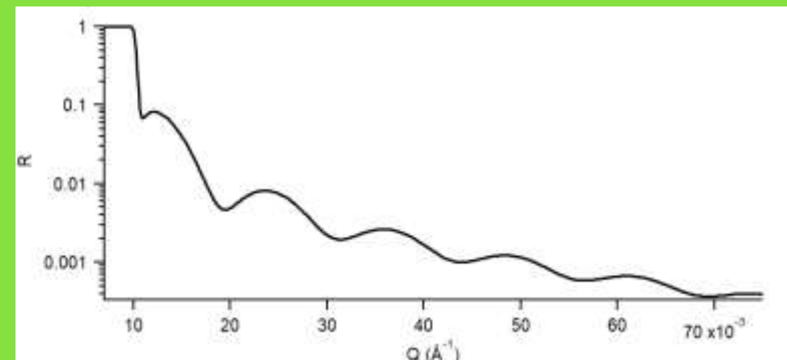
Air layer



A 500˚A polystyrene thin film that is doped with 5% mass of fullerene NPs which are combined to form a dense layer of fullerene with length δlayer = 25˚A, that is close to the fronting media. As the content of NPs in the layer ϕL = 100%, according to equation 2 this layer has SLD value ρlayer = 5.73×1010cm−2 then the film can be considered as two layers; the first one is fullerene layer which has length δC60 = 25˚A, and the second one is polystyrene layer which has length δP S = 475˚ A.



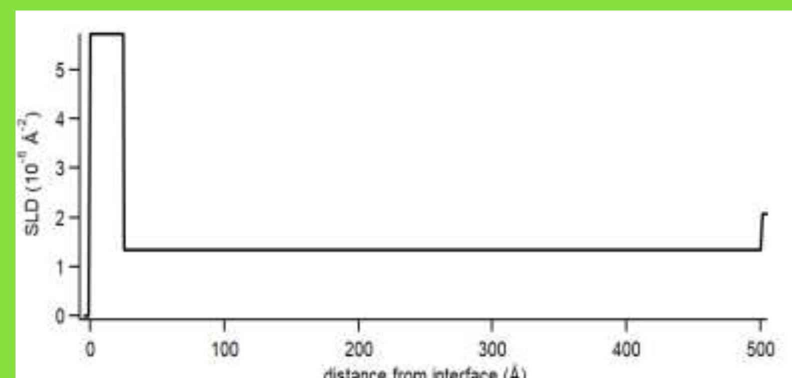


Figure 11. Reflectometry results of 500˚A polystyrene thin film, with air layer of fullerene NPs: a) reflectivity curve, b) SLD curve

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VERIFYING DATA

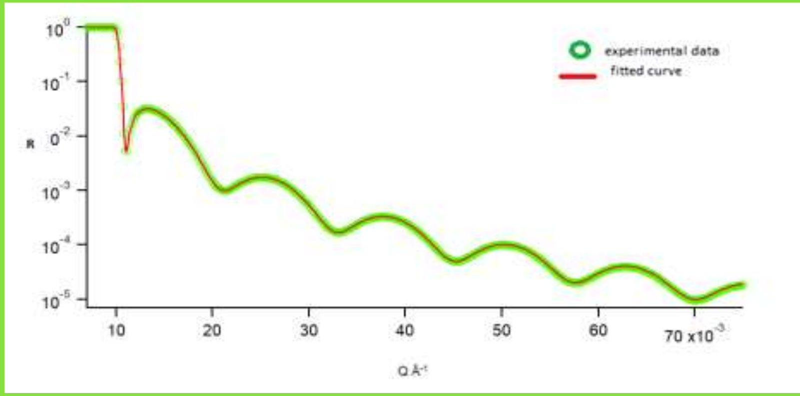
The data that is generated for the three thin films which are modeled previously are fitted as a reflectivity curve after introducing 10% error bars are introduced these error bars are symmetric, which means that it represent a systematic error. Results and graphs are found to be as follows for the three films:

1. Uniformly Distributed NPs

Based of the fitted curve the film where NPs are distributed uniformly:

- Film thickness: 499.86˚A
- Film SLD: $1.5619 \times 10^{10} cm^{-2}$
- Film roughness: 0.0175˚A
- Backing roughness: 0.0114˚A

with a value of $x^2 = 6.64 \times 10^{-11}$.



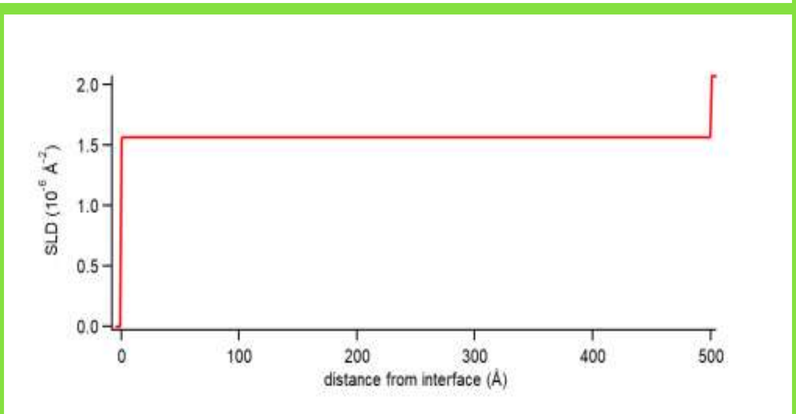


Figure 12. Fitted reflectometry curves of 500˚A polystyrene thin film, with uniformly distributed fullerene NPs, a) reflectivity curve; b) SLD curve

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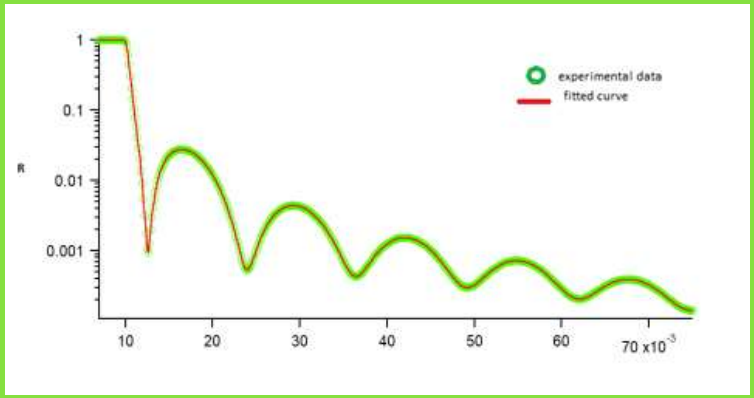
2. Substrate Layer

Based of the fitted curve the film where NPs are substrate layer,

-Film thickness: Film thickness: 499.999˚A

- First layer thickness: 475˚A
- Second layer thickness: 25.003˚A
- First layer SLD: $1.35 \times 10^{10} cm^{-2}$
- Second layer SLD: $5.7301 \times 10^{10} cm^{-2}$
- First layer roughness: 0˚A
- Second layer roughness: 0˚A
- Backing roughness: 0˚A with a value of $x^2 = 1.27 \times 10^{-10}$



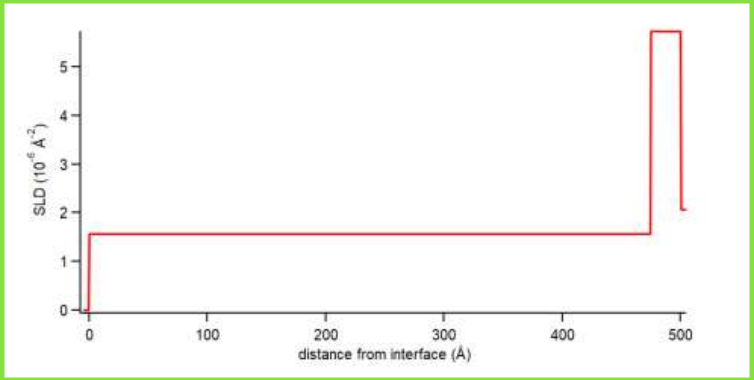


Figure 13. Fitted reflectometry curves of 500˚A polystyrene thin film, with substrate layer of fullerene NPs, a) reflectometry curve, b) SLD curve

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3. Air Layer

The film where NPs are substrate layer, has the specifications:
-Film thickness: Film thickness: 499.999˚A
- First layer thickness: 24.999˚A
- Second layer thickness: 475˚A
- First layer SLD: $5.77305 \times 10^{10} cm^{-2}$
- Second layer SLD: $1.35 \times 10^{10} cm^{-2}$
- First layer roughness: 0˚A
- Second layer roughness: 0˚A
- Backing roughness: 0˚A with a value of x^2=1.27×10^{-10}.

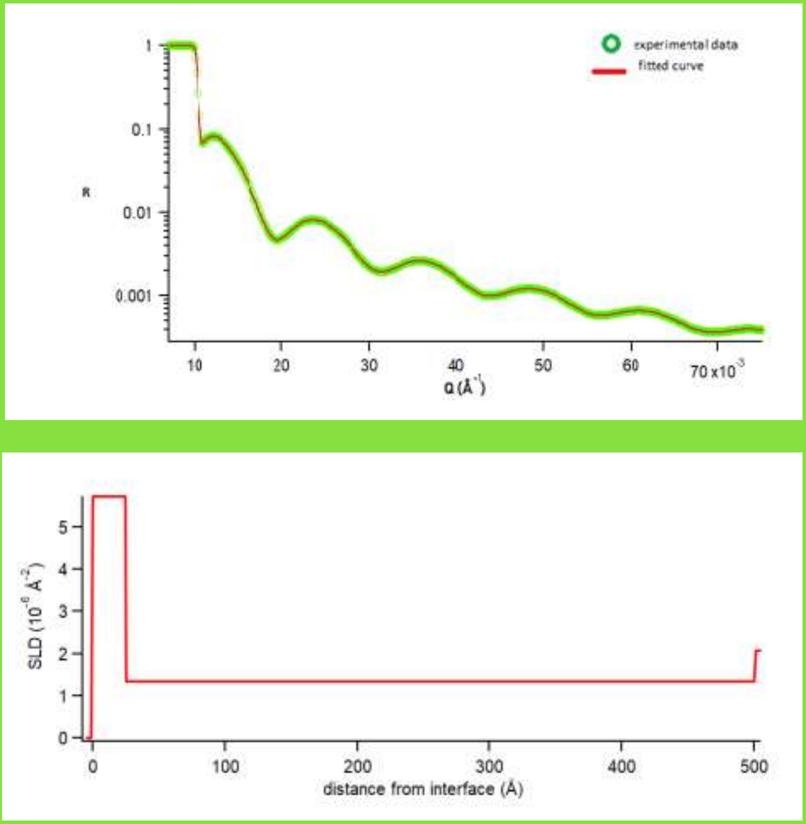

Figure 14. Fitted reflectometry curves of 500˚A polystyrene thin film, with air layer of fullerene NPs, a) reflectometry curve, b) SLD curve

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THIN FILM MODELLING (WITH ROUGHNESS)

Modelling process

Different versions of 500˚A polystyrene thin films which are doped with 5% mass of fullerene NPs C60 are modeled. Every model is characterized by NPs distribution inside the film either uniform, or substrate and air with 100% NPs content in layer.

The reflectometry experiments are designed such that the fronting media is the air with ρf ilm = 0, and Si crystal as backing media with $\rho_{film} = 2.07 \times 10^{10} cm^{-2}$ and roughness 5˚A, and the film is inserted in between, such that the polystyrene layer has roughness 10˚A, and the fullerene layer has roughness 10˚A, also . A reflectivity curve is generated for every case by generating 500 point in the range between Q = 0.007˚A^{-1} and Q = 0.075˚A^{-1}, also SLD curves are generated for every case.

The polystyrene thin film has scattering length density $\rho PS = 1.35 \times 10^{10} cm^{-2}$.

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Uniformly Distributed NPs

A 500˚A polystyrene thin film with roughness 10˚A that is doped with 5% mass of fullerene NPs which are distributed uniformly is designed. According to equation 1 the effective SLD value of the film is ρfilm = $1.569 \times 10^{10} cm^{-2}$.

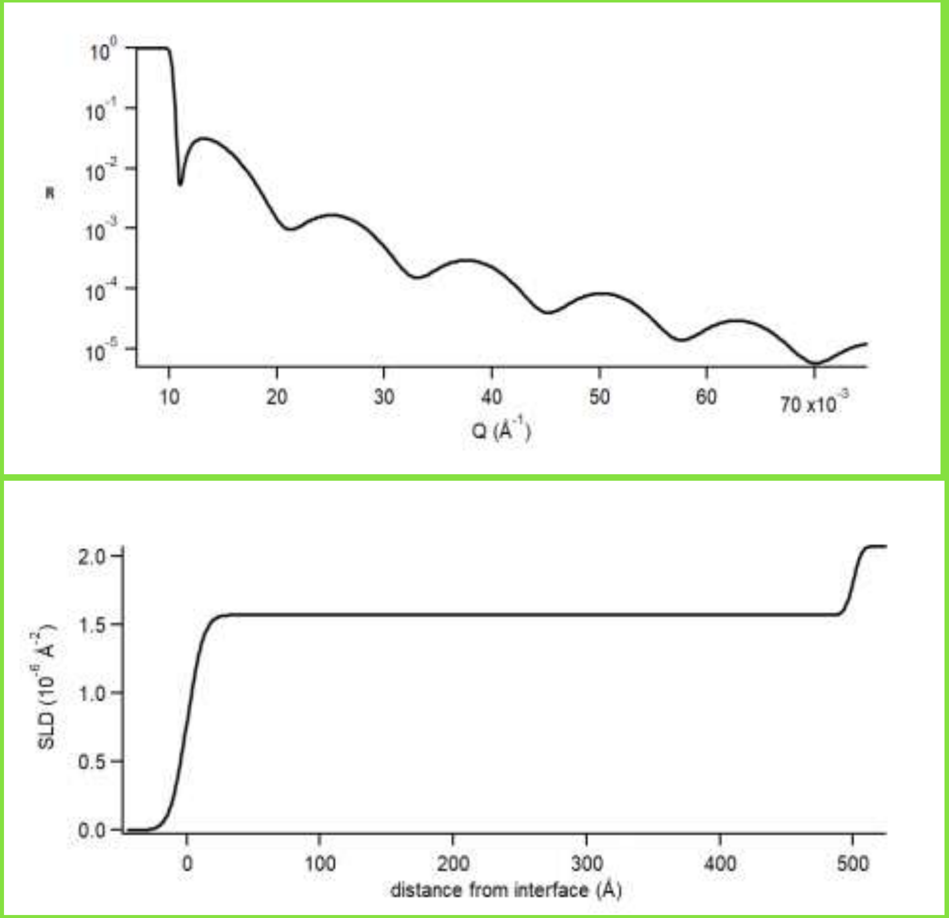

Figure 15. Reflectometry results of 500˚A polystyrene thin film, with uniformly distributed fullerene NPs, a) reflectometry curve, b) SLD curve

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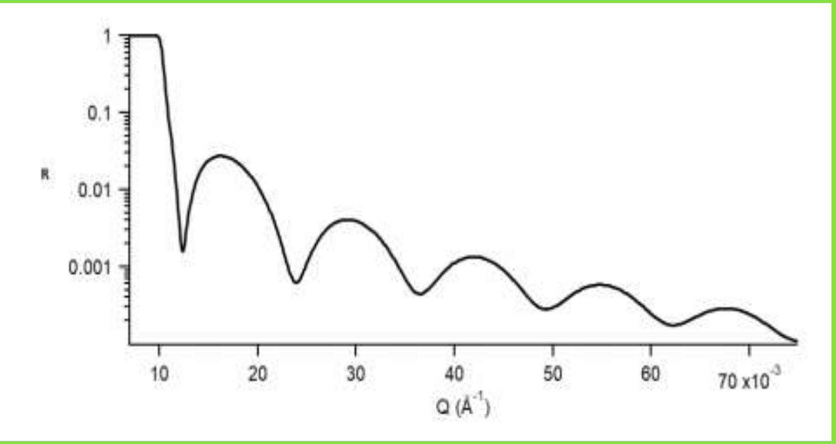
Substrate layer

A 500˚A polystyrene thin film that is doped with 5% mass of fullerene NPs which are combined to form a dense layer of fullerene with length δlayer = 25˚A, that is close to the backing media. As the content of NPs in the layer ϕL = 100%, according to equation 2 this layer has SLD value ρlayer = $5.73\times10^{10}cm^{-2}$ then the film can be considered as two layers; the first one is polystyrene layer which has length δP S = 475˚A and roughness 10˚A, and the second one is fullerene layer which has length δC60 = 25˚A and roughness 10˚ A.



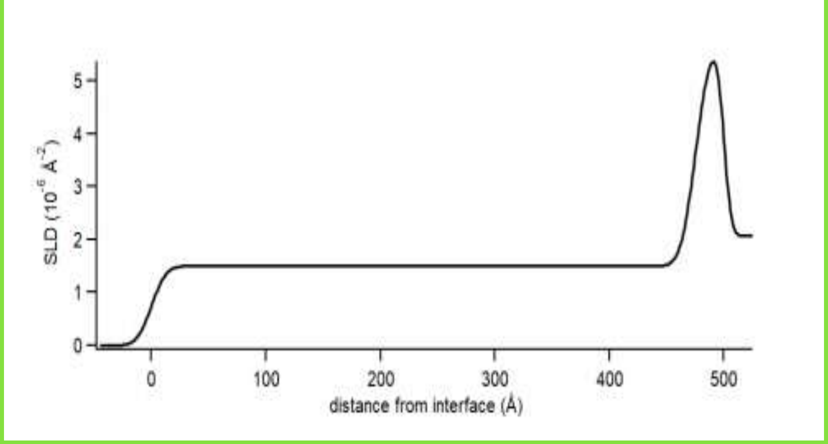
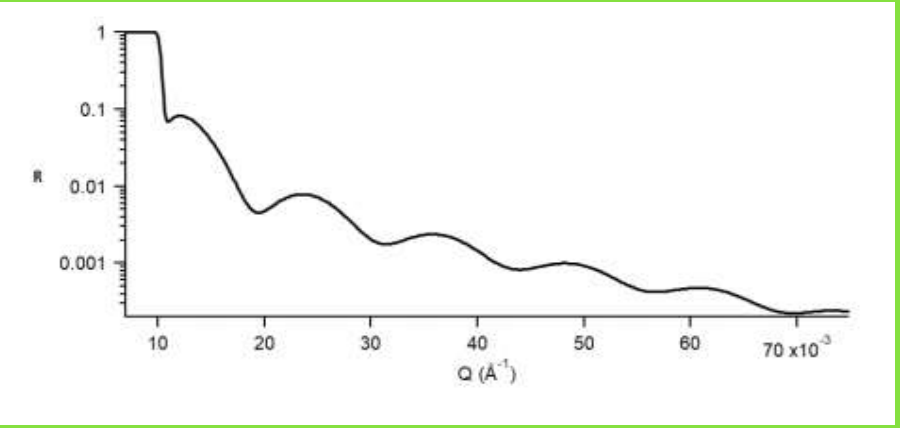


Figure 16. Reflectometry results of 500˚A polystyrene thin film, with substrate layer of fullerene NPs, a) reflectivity curve, b) SLD curve

Air layer

A 500˚A polystyrene thin film that is doped with 5% mass of fullerene NPs which are combined toform a dense layer of fullerene with length δlayer = 25˚A, that is close to the fronting media. As the content of NPs in the layer ϕL = 100%, according to equation 2 this layer has SLD value ρlayer = $5.73\times10^{10}cm^{-2}$ then the film can be considered as two layers; the first one is fullerene layer which has length δC60 = 25˚A and roughness 10 ˚A, and the second one is polystyrene layer which has length δPS = 475˚ A and roughness 10˚A.



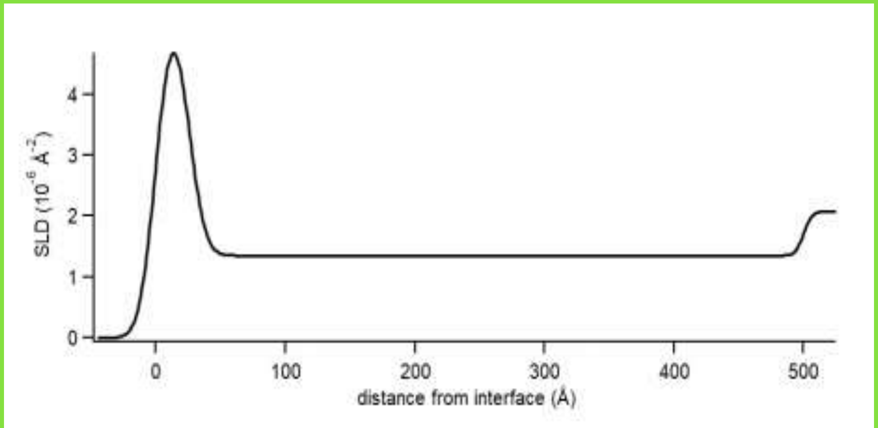


Figure 17. Reflectometry results of 500˚A polystyrene thin film, with air layer of fullerene NPs

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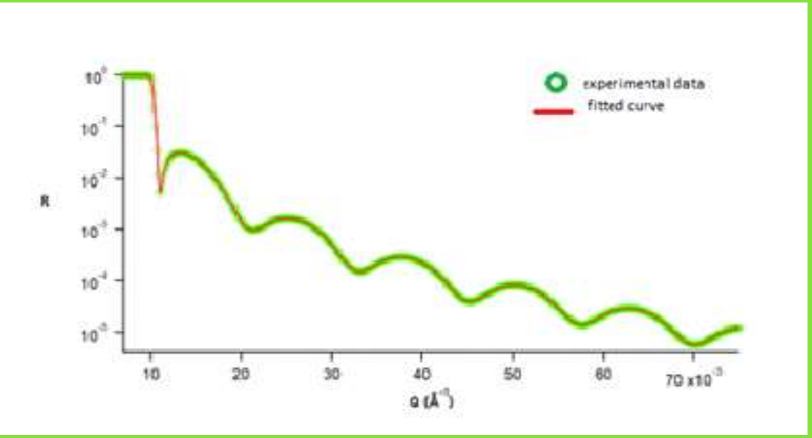
Verifying data

The data that is generated for the three thin films which are modeled previously are fitted as a reflectivity curve after introducing 10% error bars are introduced these error bars are symmetric, which means that it represent a systematic error.



Uniformly Distributed NPs

Based of the fitted curve the film where NPs are distributed uniformly

- Film thickness: 500˚A
- Film SLD: $1.569 \times 10^{10} cm^{-2}$
- Film roughness: 10.001˚A
- Backing roughness: 4.99˚A

with a value of $x^2 = 1.84 \times 10^{-15}$

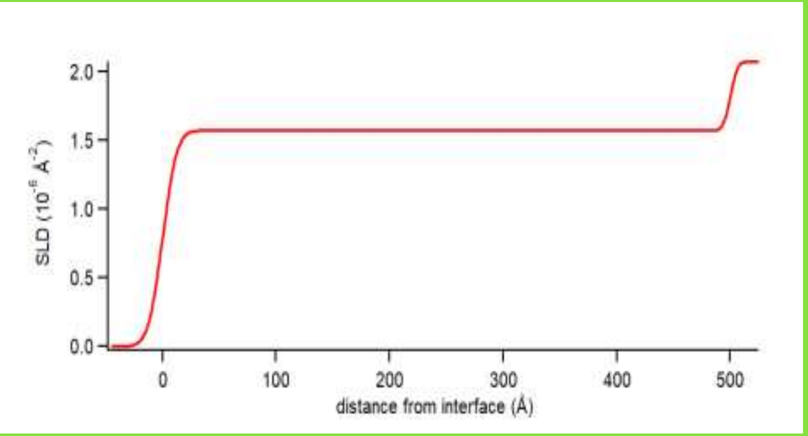


Figure 18. Fitted reflectometry curves of 500˚A polystyrene thin film, with uniformly distributed fullerene NPs, a)reflectivity curve, b) SLD curve

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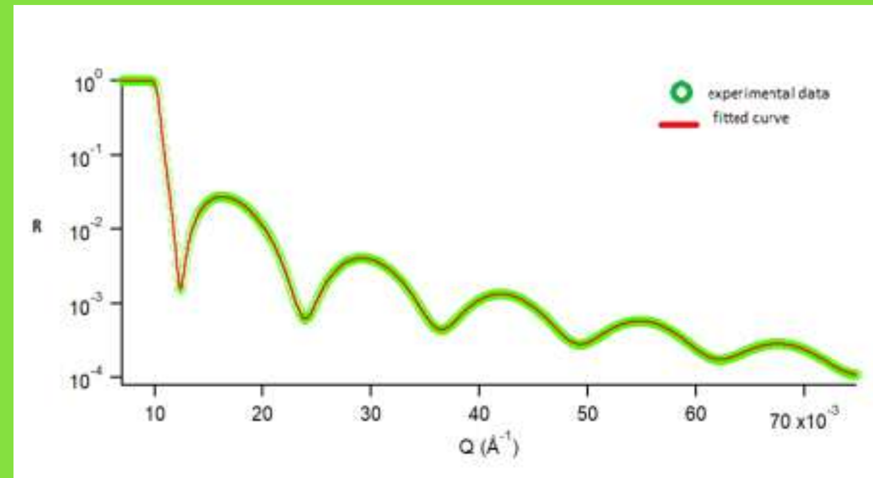
Substrate Layer

Based of the fitted curve the film where NPs are substrate layer

- Film thickness: Film thickness: 500.32˚A
- First layer thickness: 474.39˚A
- Second layer thickness: 25.962˚A
-First layer SLD: $1.4997 \times 10^{10} cm^{-2}$
- Second layer SLD: $5.583 \times 10^{10} cm^{-2}$
- First layer roughness: 10.39˚A
- Second layer roughness: 9.53˚A
- Backing roughness: 4.73˚A

with a value of $x^2 = 1.1 \times 10^{-11}$.



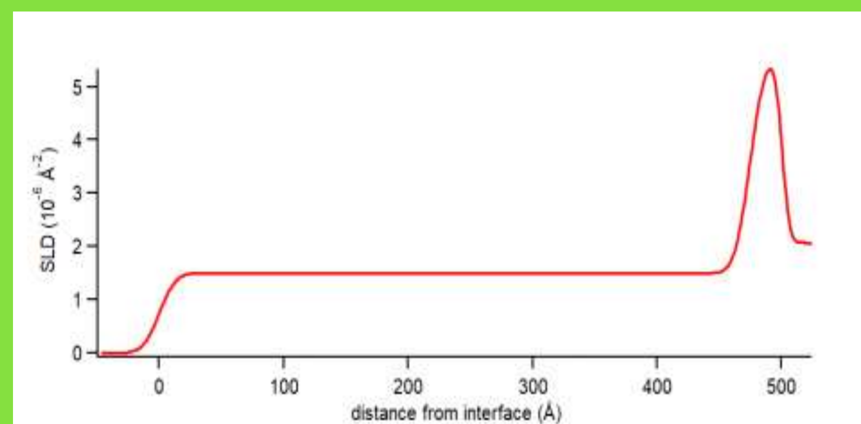


Figure 19. Fitted reflectometry curves of 500˚A polystyrene thin film, with substrate layer of fullerene NPs, a) reflectivity curve, b) SLD curve

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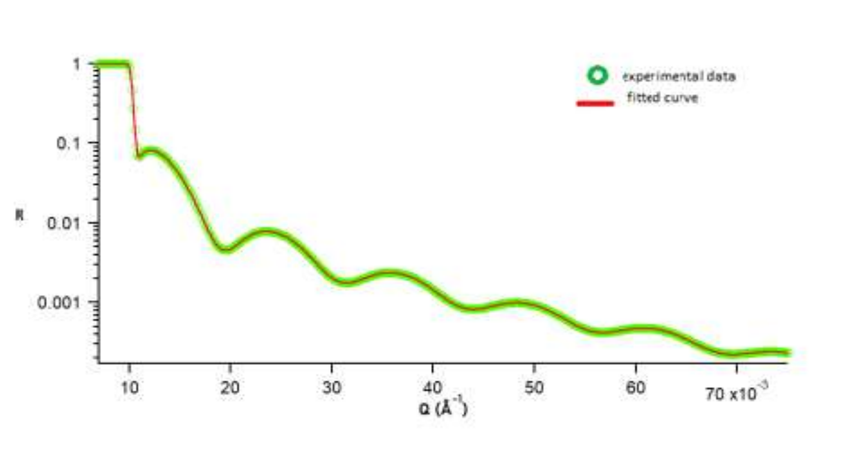
Air Layer

Based of the fitted curve the film where NPs are substrate layer:

-Film thickness: Film thickness: 499.999˚A
- First layer thickness: 24.999˚A
- Second layer thickness: 475˚A
- First layer SLD: $5.77305 \times 10^{10} cm^{-2}$
- Second layer SLD: $1.35 \times 10^{10} cm^{-2}$
- First layer roughness: 0˚A
- Second layer roughness: 0˚A
- Backing roughness: 0˚A
with a value of $x^2 = 1.27 \times 10^{-10}$.



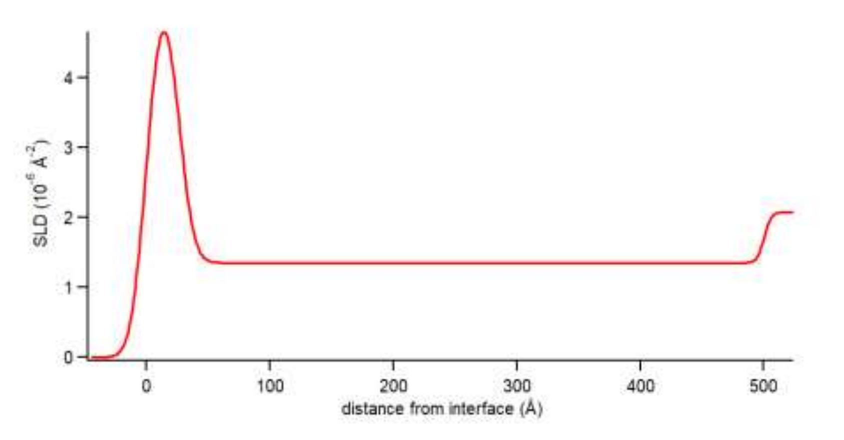


Figure 20. Fitted reflectometry curves of 500˚A polystyrene thin film, with air layer of fullerene NPs, a) reflectivity curve, b) SLD curve

CONCLUSION

Thin polymer films have numerous technological applications in various industrial and biomedical sectors related to protective and functional coatings, non-fouling biosurfaces, biocompatibility of medical implants, separations, advanced membranes, microfluidics, sensors, devices, adhesion, lubrication and friction modification.

In many cases, the films can be of complex composition with different types of polymers with complex architecture and other components such as nanoparticles.

Changes in structure of nanocomposites can be detected by reflectometry experiments of neutron/x-ray reflection by thin films which are doped with these polymer nanocomposites.

The produced models of thin films and the fitted curves shows that the smaller the content of the nanoparticles in the film, the closer the value of SLD of the film (with fullerene) to the original value of SLD of the film (without fullerene). which means that the used reflectometry experiments cannot make a conclusion about the properties of the film.

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