JOINT INSTITUTE FOR NUCLEAR RESEARCH
Frank Laboratory of Neutron Physics

FINAL REPORT ON THE INTEREST PROGRAMME

Introduction to neutron scattering experiments at large scale facilities

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1. Abstract

Neutron scattering experiments are thought to be a unique technique to investigate the structure of materials. In this report we present the advantages of neutrons and the methods in which we are able to use them in order to analyze the structure of a few experimental samples. More specific, in the first experiment we generate a tutorial by the use of the SasView software for the compound SDS (Sodium Dodecyl Sulphate). In this case, we manage to produce some calculations and finally to reach at a level where the theoretical curve of this model almost fits with the structure we chose for the SDS. The second experiment contains a proposal for the structure of the apoferritin model. We aspire to use YuMO spectrometer, IBR-2 pulsed reactor, with the intention of investigating apoferritin structure, while the theoretical estimations were done with SasView as well.

2. Project goals

The project aims to make an introduction to the field of neutron and X-ray scattering experiments at large scale facilities. Also, in this report are being presented and used the methods of SANS (Small Angle Neutron Scattering) and SAXS (Small Angle X-ray Scattering). Furthermore, it is aimed to learn about the preparation of experiments (sample preparation, proposal of experiment) and to be accustomed to a dedicated software (SasView) for data treatment and evaluation of the results.

3. Introduction

Not even a century has passed since neutrons had been reported (1932) by James Chadwick, a significant discovery which led him to win the Nobel Prize in physics in 1935. He came up with the idea of using a polonium source to irradiate beryllium nuclei with α-particles. The discovery of neutron gave a huge impulse to the elaboration of Nuclear Physics, whereas after that pursued the discovery of fission, the nuclear chain reaction and of course the construction and function of the first nuclear reactor (Chicago Pile-1) by the leadership of Enrico Fermi.

According to quantum mechanics, neutrons appear to have both particle-like and wave-like properties. These properties are:

- Mass: $m_n=1.675\cdot10^{-27}$ kg=939.57 MeV/c^2.
- Electrical charge: q=0 (some experimental measurements showed that if neutrons have electrical charge, this must not exceed the limit of 10^{-18}e, where e is the electrical charge of electrons).
- Lifetime: $t_{1/2}$=879.6±0.8 s (free-unstable neutrons, outside the nucleus).
- Magnetic dipole moment: $\mu_n=-1.913\cdot\mu_N$, where μ_N is the nuclear magneton.
- Spin: s=1/2 (due to its charge distribution).
- Wavelength: λ (nm) =395.6/v (m/s).
- Energy: E (meV) =0.02072k^2 (k in nm^{-1}).

On the other side, we have X-rays, which is a type of high energy electromagnetic radiation with frequencies in the range of $30\cdot10^{15}$ Hz to $30\cdot10^{18}$ Hz, so in the electromagnetic spectrum they stand between UV light and gamma-rays. X-rays were discovered by Wilhelm Conrad Röntgen in 1895 and the very first Nobel Prize was awarded to him in 1901 for this contribution.

In this project we use neutron scattering in order to determine the positions and motions of atoms in condensed matter. Neutrons have some remarkable advantages, such as:

- Wavelength comparable to interatomic spacing.
- Kinetic energy equal to that of atoms in solid.
- Penetration properties, without damaging the sample.
- Weak interaction with matter aids interpretation of scattering data.
- Isotopic sensitivity allows contrast variation.
- Neutron magnetic moment couples to B, so neutron sees unpaired electron spins.

Of course neutrons have also disadvantages. Briefly, these include the weakness of neutron sources (low signals, need for large samples), the strong absorption of some elements (Gd, Cd, B) and kinematic restrictions (cannot access all energy and momentum transfers).

4. Methods

Neutron scattering experiments measure the number of neutrons scattered by a sample as a function of the wavevector charge (Q) and the energy change (E) of the neutron. The scattered neutron intensity as a function of Q and E is proportional to the space and time Fourier Transform of the probability of finding two atoms separated by a particular distance at a particular time.

Neutron diffraction is used to measure the differential cross section $d\sigma/d\Omega$. In fact it is a technique to measure the static structure of materials ranging from crystalline solids and amorphous materials to larger structural sizes.

Small Angle Neutron Scattering (SANS) is used to measure large objects on length scales from 1 nm to 1 μm. SANS is sensitive not only to light elements such as H, C, N but also to isotopes such as H and D. With SANS we do not aspire to approach the atoms scales, but we are able to observe the organization of particles in dispersed systems. This transpires due to the great size of the materials used (proteins, micelles, polymers etc.).

Neutron Reflectometry is a technique to measure the structure of thin films and it provides the opportunity to study solid/solid, solid/liquid, liquid/liquid and liquid/air interfaces. It probes relevant lengths (from Å to μm), it is sensitive to light elements (H, C, O, N), it is a non-destructive technique and gives the probability of isotopic labelling (which plays an indispensable role in structure determination of proteins and biomacromolecules).

Neutron Spectroscopy is a method to measure the atomic and magnetic motions of atoms and molecules. It probes the dynamics of magnetic moments, molecules and lattices over length scales ranging from a few Å to tens of nm. Inelastic neutron scattering observes the change in neutron energy as it scatters from a sample.

In continuous reactors we are able to achieve only a few improvements in fluxes, because of the saturation of the technology, as we have a limit of heat removal rate and operating safety considerations. On the other side, pulsed sources are expected to go to higher fluxes, as the non-continuous operation allows for a better heat removal rate. Continuous reactors operate in a continuous neutron generation mode, whereas spallation sources function in a pulsed mode (time of flight or TOF).

5. Experiment I: The tutorial

For the objective of analyzing experimental data and present an experimental data evaluation of sample systems, we use SasView. It is a software for the analysis of Small-Angle Scattering (SAS) data, it fits analytic functions describing different types of material microstructure to experimental data in order to determine the shape, size and degree of ordering. Furthermore, it includes tools for calculating scattering length densities, slit sizes, resolution, fringe thicknesses/d-spacings, the (Porod) invariant (total scattering), and distance distribution functions.

At this point, it is going to be presented an example with the use of the aforementioned software, SasView. For this purpose, we utilize our techniques to the surfactant h25-SDS (sodium dodecyl sulphate) as a 2% solution in D_2O (deuterium oxide/heavy water).

To begin with, we have to start the application SasView. Then, from the Data Explorer panel we load the data we want to analyze, so we choose from the folder \test\1d_data the intended compound, which in our case is hSDS_D2O_2p0_percent.xml and press open. Hereupon, from the Data Explorer we select the option Fitting and Send data to begin the process of fitting.

Now, in the Fit Page has loaded our chosen compound, so it is ready for processing. From the theory we know that SDS micelles are considered approximately spherical in the absence of electrolyte, so for our model we choose the category ‘sphere’ and for the model name ‘sphere’ too. As we can see, 5 parameters have been opened in the Fit Page, 2 general (scale and background) and 3 for the selected model (sld, sld solvent, radius). It is time to use the SLD (scattering length density) Calculator, which is an important tool for calculating neutron scattering length densities of a given chemical formula. For this reason, we visit the Menu Bar, we select Tools and finally we pick the SLD Calculator. In the emerging window, we insert the molecular formula and the densities in the relevant boxes, while we leave the neutron wavelength constant in the value of 6.0 Å. So we fill in the appropriate blanks with the formulae Na1C12H25S1O4, D2O1 and densities 1.01, 1.11 respectively. The tool does automatically the calculations and in the output emerges the Neutron SLD result, which is sld=$0.337 \cdot 10^{-6}$ Å (for the SDS) and sld_solvent=$6.39 \cdot 10^{-6}$ Å (for the D_2O).

We enter these values in the Fit Page and then we check the boxes alongside scale, background and radius and we click the Fit option. The graphical representation obtained is presented in Figure 1:

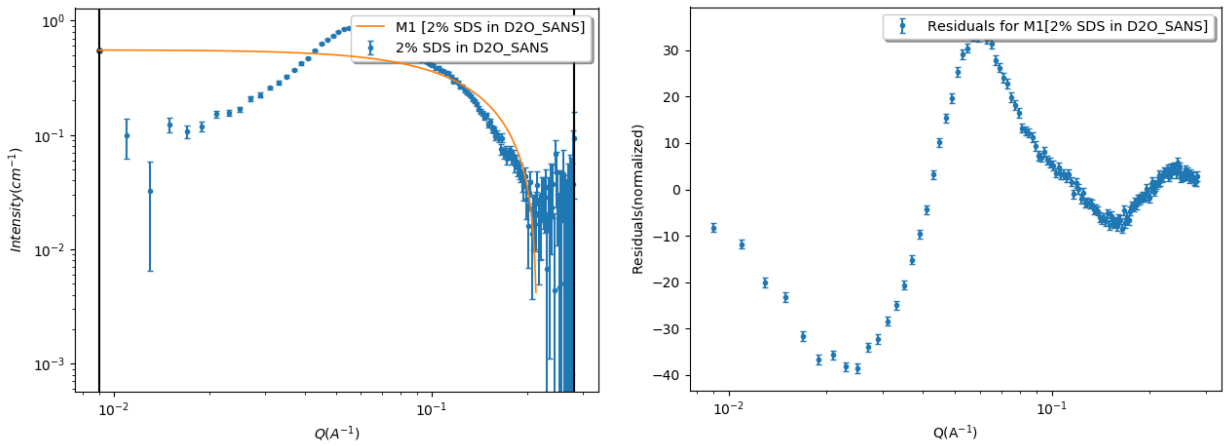

Figure 1: Plots of Intensity-Q and Residuals(normalized)-Q for the compound hSDS_D2O_2p0_percent with X^2=198.58.

The orange is the theoretical curve for scattering from non-interacting, monodisperse, spherical micelles with 12.934 Å radius. As we observe, there is not a very good fitting, something that can be confirmed with the value of the fitting error (reduced X^2), which is 198.58, whilst should be around 1. Well, this is our purpose, so we need to reduce X^2 or in other words we have to improve the fitting of the blue and orange curves.

To do this we can start by incorporating the right Structure Factor of the model, which in our case is hayter_msa (Hayter-Penfold Rescaled Mean Spherical Approximation). This adds 5 more parameters for the model, the volfraction, charge, temperature, concentration_salt and dielectconst. The volfraction parameter duplicates the scale parameter, so we set the scale 1.0 and we uncheck it so that it does not affect the graph. Moreover we make changes for the values of some parameters as follows: volfraction=0.019, temperature=298 K, concentration_salt=0 M, dielectconst=78.06, radius=17.701 and background=-0.023534. After we execute the Fit, we obtain the following graphs (Figure 2):

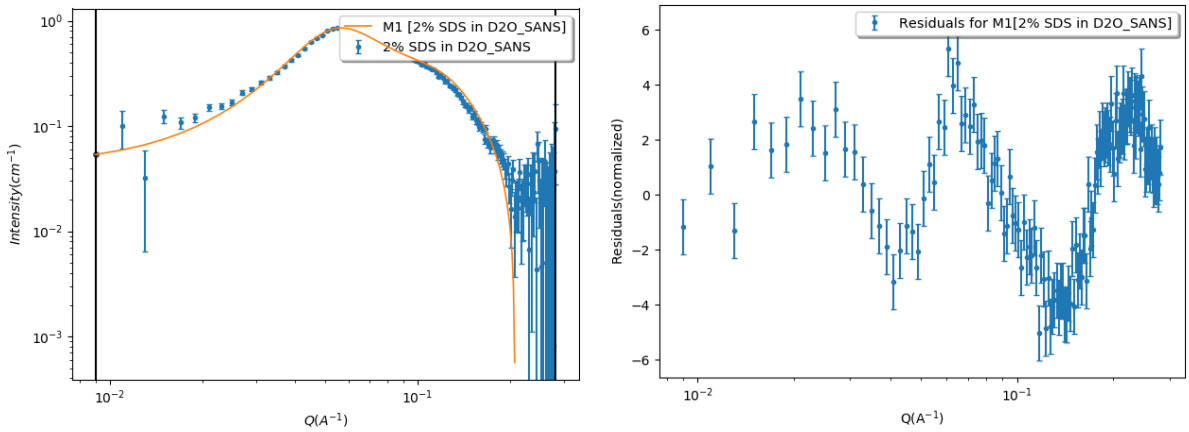

Figure 2: Plots of Intensity-Q and Residuals(normalized)-Q for the compound hSDS_D2O_2p0_percent with X^2=6.3519.

We notice that the fitting error in this case is much lower, X^2=6.3519, and in the graph the blue curve seems much closer to the orange. So we begin to reach our goal, but we need a few more details fixed in order to fit perfectly.

In order to make an improvement to our model, we suggest that the water molecules are mixed in with the surfactant sulphate head groups. This means that the effective SLD of the surfactant molecules is being increased, while the scattering contrast (sld, sld_solvent) is being reduced. Therefore, we check the box next to the sld parameter and the results are below (Figure 3):

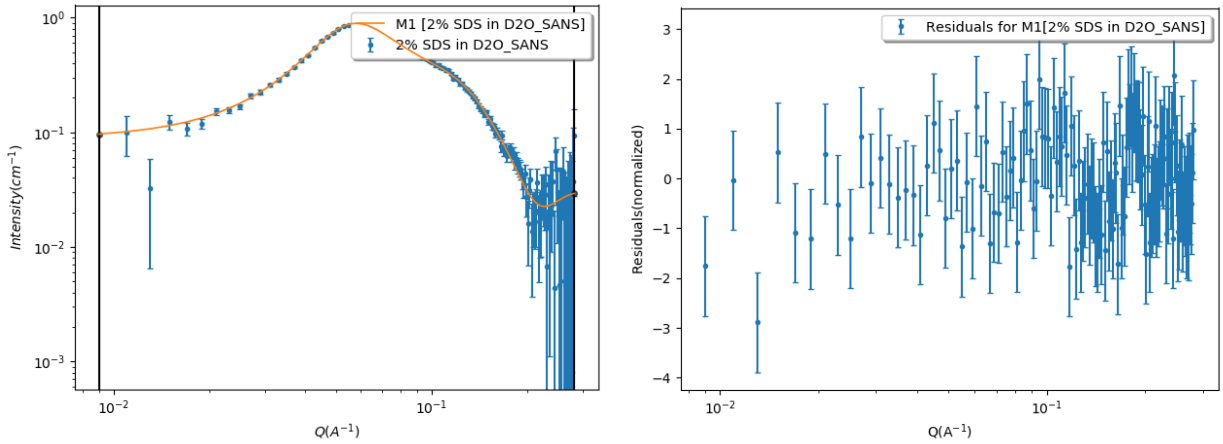

Figure 3: Plots of Intensity-Q and Residuals(normalized)-Q for the compound hSDS_D2O_2p0_percent with X^2=0.85581.

As we observe, the two curves almost osculate one another and the reduced chi-square is X^2=0.85581, so our goal has mainly been accomplished.

Now, in our last effort to approach the best possible fitting, we make a different assumption. We suggest that SDS micelles are actually ellipsoidal, so we choose the Ellipsoid in the Category, the ellipsoid in the Model name and the hayter_msa for the Structure factor. For the hayter_msa we set the same values as before and then we set the scale equal to 1.0, the volfraction 0.017 and the charge 20. The checked parameters are: background, sld, radius_polar, volfraction and charge.

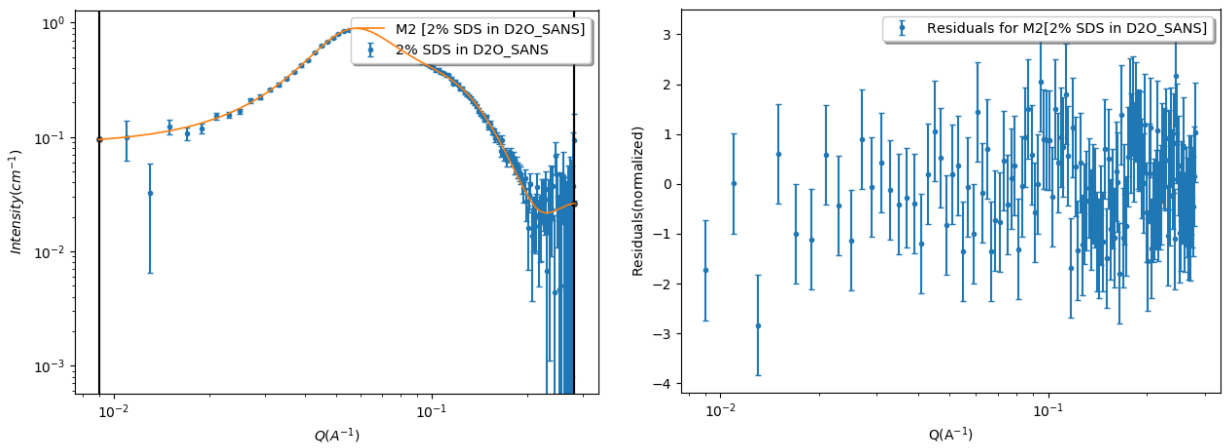

Figure 4: Plots of Intensity-Q and Residuals(normalized)-Q for the compound hSDS_D2O_2p0_percent with X^2=0.96181.

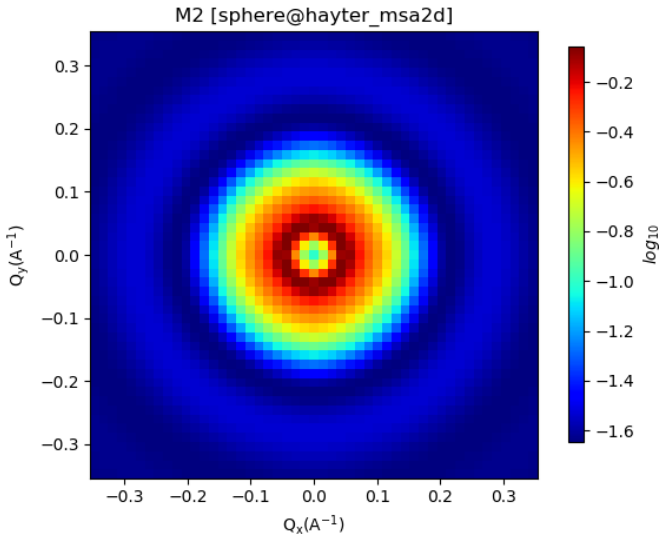

Figure 5: 2-D diffraction image for the compound hSDS_D2O_2p0_percent with X^2=0.96181.

Inferentially, we loaded a compound to the Fit page and we started setting the parameters in order to achieve a better fitting. With the setting of the appropriate model and the proper structure factor, we reduced the chi-square and we reached it very close to the desired value, which is 1. In our first three attempts we assumed a spherical model and the X^2 came down to 0.85581, but in the last one we assumed an ellipsoid model with hayter_msa as a structure factor and X^2 equal to 0.96181. In both cases we obtained very good fitting, however the ellipsoid model with an axial ratio of 1:1:2 seems to have the best possible fitting and chi-square. It is a fact that we should have more meticulous measurements and higher quality data for the purpose of acquiring better knowledge and clear view of the models.

6. Experiment II: The proposal

Aim of the proposed experiment and description of the scientific background

In this Experiment II we are working with the compound apoferritin, which is indispensable for almost all living organisms, including animals, higher plants and bacteria. More specific, apoferritin is a protein, which is mainly present in the intestinal mucosa membrane. It has a very important role of binding and storing iron by combining with ferric hydroxide-phosphate, resulting in the formation of the compound ferritin. In order to understand the significance of ferritin and by extension of apoferritin, we should mention that this protein is found in most tissues and it is generally an indirect indication of the total amount of iron stored in the organism (iron-deficiency anemia can usually be diagnosed by the levels of ferritin in blood).

The aim of this experiment is to determine the structure of raw horse spleen apoferritin on a low resolution instrument. For this purpose, we analyzed apoferritin with SasView in order to have an a priori knowledge of its structure.

Table 1: The core_multi_shell spherical model of apoferritin.

Parameter	Value	Error	Units
scale	0.011751		
background	0.03	9.0988e-05	cm^{-1}
sld_core	173.89	0.065693	10^{-6} Å^{-2}
radius	20.426	0.172	Å
sld_solvent	172.45	0.0022008	10^{-6} Å^{-2}
sld1	171.91		
thickness1	47.624		
Fitting Error X^2	1.9992		

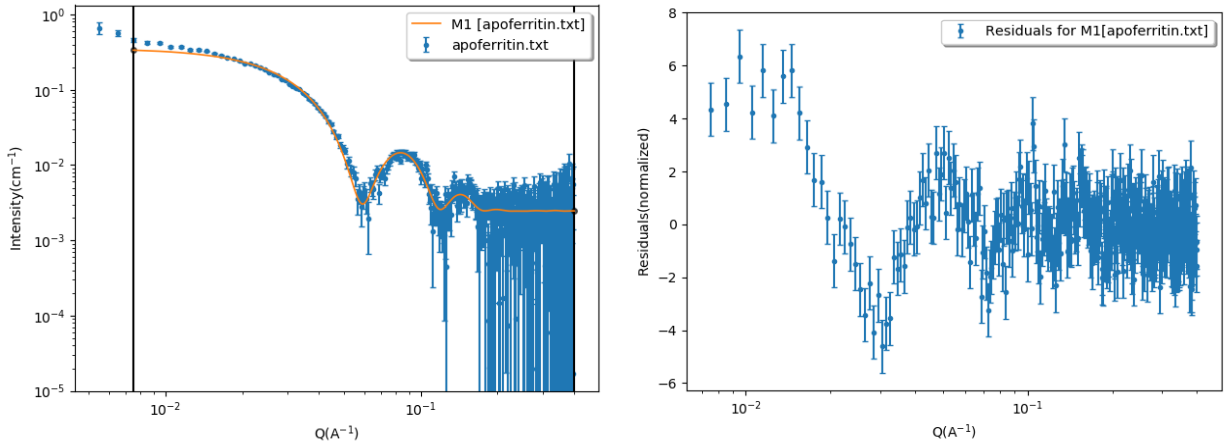

Figure 6: Raw apoferritin curves, as core_multi_shell spherical model.

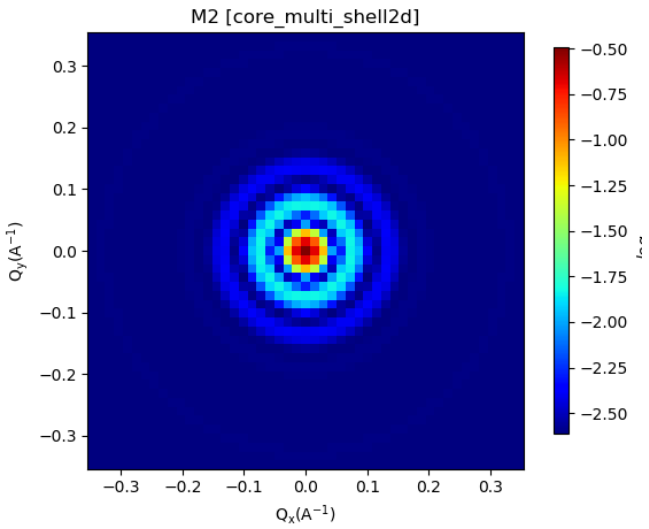

Figure 7: Raw apoferritin diffraction image.

We suggest that apoferritin appears generally as a spherical model and particularly it develops multiple shells around its core, so we chose core_multi_shell for its model name. The exact values of the parameters are presented in Table 1 and the curves obtained, can be observed in Figure 1.

Details of the neutron experiment

The experiment is proposed to be performed at YuMO spectrometer, IBR-2 pulsed reactor, Frank Laborator of Neutron Physics. As it is a SANS experiment, this is the appropriate instrument. YuMO uses thermal neutrons with flux of 10^7- $4{\cdot}10^7$ n/(s cm^2), the wavelength ranges from 0.5 Å to 8 Å, the size of beam on the sample will have 14 nm diameter and vanadium is the calibration standard.

We prefer to use neutron scattering because of the desirable properties neutrons exhibit. In other words, we can penetrate the sample without damaging it and furthermore neutrons have a comparable wavelength to interatomic spacing, so we are able to observe the structure of a material.

The mean beam time for the measurement of one sample is approximately 1 hour. Just to reduce any random errors, we aspire to measure three samples, so in this case we need 3 hours for the whole process.

Expected results

From this experiment we anticipate to obtain a scattering curve (experimental), whose

correspondence will be very close to the theoretical model we suggested (Figure 1). If this happens and the two curves fit perfectly, we will assume that apoferritin has a spherical core_multi_shell structure. In any other case, we will have to evaluate the experimental results and reconsider the structure of our compound. However, as there have been reported many studies and experiments with apoferritin, there are indications that this proposal cannot be far from the truth.

7. Acknowledgements

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