KWS-1 & KWS-2

Small Angle Neutron Scattering

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Manual of the JCNS Laboratory Course Neutron Scattering

Contents

Fig. 1: *Representation of the protein lysozyme, which has a very compact form.*

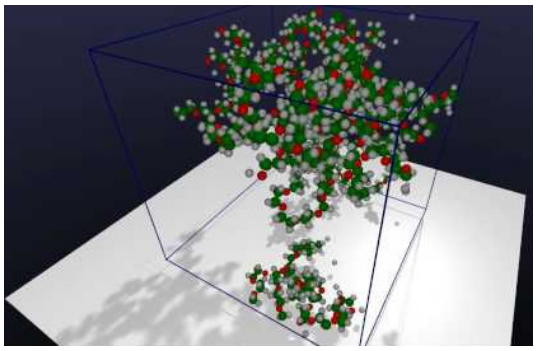

Fig. 2: *Molecular dynamics conformation of poly ethylene oxide in solution.*

1 Introduction

The objective of this lab course is to clarify the essential concepts of small-angle neutron scattering. Structures are only visible by a scattering experiment if there is an appropriate contrast. For neutrons one often uses the exchange of ^{1}H by ^{2}H, i.e. deuterium. The contrast of this lab course is achieved by using heavy water (D_2O) as solvent. The materials (solutes) are natural ones having normal protons.

The globular, compact lysozyme (Fig. 1) appears in chicken eggs and has anti-bacterial function. The molecule is charged, which leads to repulsive interactions. So there is a short range order, and the distance between the molecules can be determined.

The other molecule is the synthetic poly ethylene oxide (Fig. 2) with the chemical formula of $[\text{-}CH_3\text{-}CH_3\text{-}O\text{-}]_n$. It is one of the simplest water soluble polymers. The hydrogen bonds of the oxygen are responsible for attractive interactions between water and the polymer. The molecules form rather dilute coils in solution and the overall dimension of the coil will be determined by SANS. Furthermore, the fractal structure of the coil will be determined.

2 Preparing solutions in Water

A lysozyme solution of 0.02g per ml of water must be prepared. We will weigh 0.02g of Lysozyme and put it into a new Packard glas. With an Eppendorf pipette we will add exactly 1 ml D_2O. These pipettes are extremely accurate with respect to the volume. From the solution about 0.5 to 0.6ml are transferred to Hellma quartz cuvettes, which are 1mm thick. For the later evaluation we need a highly accurate concentration. So all weights need to be written down as exactly as possible.

For the poly ethylene oxide solution we chose the same concentration. Since the polymer exists

in small platelets the tiny amount of polymer will not be that accurately prepared. Corrections can be either done by chosing a different volume of heavy water or by just writing down the exact weights. However, stay below 0.04g/ml for the concentration!

3 The Measurement at KWS-1 and/or KWS-2

These two solutions are now being measured in the small-angle neutron scattering instrument KWS-1 (or KWS-2). The wavelength of neutrons is set to 7Å. The collimation is fixed to 8m. The samples are placed as close as possible to the detector, to measure the largest Q values possible. Both samples will be measured at detector distances 2m and 8m. The offset between the sample position and the detector of about 30cm leads to effective detector distances of about 1.7m and 7.7m.

The sample holder will be filled with the two samples. In addition, the empty beam and a plexiglass plate are measured for absolute calibration. For a good statistical measurement the following times are set: 8m detector distance for 20min, and 2m detector distance 10min. The total measuring time for the 4 positions will be about 2 hours. The measurement is typically started before lunch, and can be evaluated in the afternoon. It is quite likely that an internal employee will start separate measurements during the afternoon until the next morning in order to use the valuable measuring time overnight.

4 Evaluation of the Scattering Data: Absolute Calibration

The measured data is raw data at first and describes the intensity on the detector. The data has to be corrected for the effectiveness of the different detector channels. Then the empty beam measurement is subtracted to account for the zero effect of the instrument. Then the intensities are expressed as absolute units using Eq. 5.5 and are radially averaged, because for the isotropic scattering samples, the intensity does not depend on the polar angle. To perform all these steps we will be using a software available in our institute, called QtiKWS. However, since the understanding of the Eq. 5.5, as such, is more important than the exact technical understanding of the evaluation, the results are produced relatively quickly by the software, namely, $\mathrm{d}\Sigma/d\Omega$ as a function of the scattering vector Q for our samples. This data will be provided for the students to do the final evaluation. In the following, this evaluation is described.

5 Evaluation of Lysozyme Scattering Curves

The position of the maximum $Q_{\max}$ provides information on the typical distance of the proteins in solution. This can be calculated to $\ell = 2\pi/Q_{\max}$. Knowing the weight of the protein in water (0.02g/cm^3) there is an alternative way to calculate the average distance. The molar mass of the protein is 1.43×10^4g/mol. The number density of the protein is therefore $n/V = 0.02\text{g/cm}^3/(1.43 \times 10^4\text{g/mol}) = 1.40 \times 10^{-6}\text{mol/cm}^3 = 8.42 \times 10^{-7}\text{Å}^{-3}$. For a simple cubic packing the typical distance is given by $\ell = \sqrt[3]{V/n}$. For a hexagonal close packed lattice the

typical distance is $\ell = \sqrt[6]{16/27}\sqrt[3]{V/n}$. This distance is the minimum distance of the planes important for the scattering experiment, and the next neighbor distance of the hexagonal c.p. lattice is $\sqrt{3/2}\,\ell = \sqrt[6]{2}\sqrt[3]{V/n}$. Both calculated distances of the cubic and hexagonal structure are to be compared with the measured one.

6 Evaluation of the Polymer Scattering

In a first step we have to prepare the scattering data for background subtraction. We plot the original data of the two detector distances in a log-log plot, i.e. $\log_{10}(d\Sigma/d\Omega) \rightarrow \log_{10} Q$. After this, we will see a plateau at high Q which indicates the constant incoherent scattering. Taking the average of the last (say 10) points will give us the estimate of the background. A new column with the background subtracted will be generated for the 8m and 2m measurements. Finally, the two data sets should be combined to yield a single data set.

Now, we will aim at the overall appearance of the chain, i.e. we will determine the chain dimension. For this purpose the Guinier approximation can be applied. The general appearance of the Gunier scattering law was already given in eq. 5.35 and reads:

$$\frac{d\Sigma}{d\Omega}(\mathbf{Q}\rightarrow 0) = \frac{d\Sigma}{d\Omega}(0) \cdot \exp\left(-\frac{1}{3}Q^2R_g^2\right) \tag{1}$$

For this purpose we plot the logarithm of the background corrected intensity against the square of the scattering vector, i.e. $\ln(d\Sigma/d\Omega) \rightarrow Q^2$. The highest Q will lead to large values that we are not interested in. So the plot has to be truncated to the rather small Q, say $Q^2 = 0..4 \times 10^{-4}\text{Å}^{-2}$. Here, we do a linear regression and take the slope S as a result only. It has the units Å^2. From this we can calculate the radius of gyration using $R_g = \sqrt{-3S}$. From previous measurements we know that it is roughly 60Å large.

For the fractal structure we plot the data in a log-log plot again (background corrected). There is the Gunier region indicated by flat scattering at low Q. At high Q the data will have very large noise, and maybe negative values might appear from the subtraction. In the middle, the scattering should be linear, indicating a power law characteristic for fractal structures. Again, we use a linear regression to determine the slope α. From the ideal polymer without interactions we learned that the exponent would read $\alpha = 2$ (see eq. 5.50). When taking the attractive interactions of the solvent into account, the exponent would be rather $\alpha = 1.70$. The reciprocal value α^{-1} is called Flory exponent and takes the ideal values of 0.5 or 0.588 for non-interacting chains and chains in a good solvent, respectively. Please make your own judgement!

7 Preparatory Exercises

(I) Lysozyme in D_2O

The first sample of the Neutron Lab Course at the SANS instrument KWS-1 (KWS-2) will be Lysozyme in heavy water (D_2O). This protein is rather globular (diameter ca. 5 nm). The Coulomb interactions of this charged molecule lead to liquid-like short-range-ordering. This will be observed in the SANS scattering experiment by a correlation peak. Simple estimations will be made now:

1. Give the connection between the number density ϕ and the unit cell parameter assuming a simple cubic lattice!
2. The chemical concentration c is usually given in g/L or mg/ml. The molar mass of the molecule is 14307g/mol. What is the connection between the chemical concentration and the number density?
3. The correlation peak appears at a scattering vector $Q_{\max}$. How would it relate to the unit cell parameter of a simple cubic lattice? What is the dependence of $Q_{\max}$ as a function of the chemical concentration c?
4. Please rationalize the relations of the hexagonal close packed lattice with respect to the cubic packing! The spacing of the planes is shorter by a value of rougly 0.916 (larger Q value compared to cubic). The nearest neighbor has a larger distance of ca. 1.122 times the cubic packing.

(II) Polymer in Solution

We will look on the overall dimension of the chain and on the fractal structure of the chain.

1. The Appendix B derived the Guinier scattering law for any shape of particles while in the main manuscript the first application was the compact sphere. How has the compactness of a polymer in a good solvent to be seen? Is there any restriction for the Gunier scattering for polymers?
2. At large Q we observe a constant background from incoherent scattering. The hydrogen atom has a incoherent cross section of 80×10^{-24}cm^2, and the deuterium atom 2×10^{-24}cm^2. The concentration of hydrogen from the polymer is roughly 50 times smaller than the concentration of deuterium from the heavy water. On the basis of these numbers estimate the ratio of background from the polymer and the solvent!
3. The fractal structure means that looking inside a coil still finds the situation of the connectivity of a chain on smaller length scales compared to the overall chain. The chain is self-similar on length scales (between the overall coil dimension and the monomer dimension). The different exponents α of 2 and 1.7 for ideal chains and polymers in a good solvent describe different compactness of the structure. Rationalize the difference between a non-interacting chain and a chain that "feels" its own presence!

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