Evaluation of solution stability for two-component polydisperse systems by small-angle scattering

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Abstract. The article is devoted to the modelling of small-angle scattering data using the program MIXTURE designed for the study of polydisperse multicomponent mixtures. In this work we present the results of solution stability studies for theoretical small-angle scattering data sets from two-component models. It was demonstrated that the addition of the noise to the data influences the stability range of the restored structural parameters. The recommendations for the optimal minimization schemes that permit to restore the volume size distributions for polydisperse systems are suggested.

1. Introduction

A number of nanoparticle systems that form polydisperse mixtures in solution are of great interest to industrial, medical and biological applications [1-5]. However, the analysis of these systems is not always straightforward. Small-angle scattering (SAS) is the effective structural method to quantitatively investigate the behavior of complex multicomponent systems in solution. Earlier the program MIXTURE [4] that belongs to the package ATSAS [2, 3] was developed. This program allows one to analyze multicomponent systems containing various types of polydisperse particles and take into account the interparticle interactions.

Normally the analysis of experimental SAS curves is carried out using the following scheme: an appropriate theoretical model that depends on a finite number of structural parameters is selected and an iterative minimization process is used to optimize a given set of parameters that minimizes the difference between the experimental data and the calculated data from the theoretical model.

However, the non-linear dependence of the parameters complicates the search of the global minimum of the target minimization function. In a standard approach the range of possible values is defined for each parameter and the solutions are searched within this range. The solutions may often differ significantly from each other. It depends on the complexity of the model, the initial search values of the parameters and the noise of the experimental data. Therefore, the analysis of the solution stability plays an important role for the reliable restoration of the theoretical model.

In this study we performed the simulation of the theoretical data sets using the program MIXTURE and evaluated the stability of the solutions from the systems consisting of two types of spherical particles. The structural parameters describing the system were randomly changed and the correctness of
the restored solution was checked. In addition, the noise with different relative levels was added to the theoretical data sets and its influence on the solution stability was studied.

2. Small-angle scattering intensity from multicomponent polydisperse system

The scattering intensity of the multicomponent system (without the interparticle interference) can be represented as a linear combination of the individual components:

$$ I(s) = \sum_k v_k I_k(s), $$

where the sum goes over different components, $v_k$ and $I_k(s)$ are the volume fraction and the scattering intensity from the $k$-th component, respectively, $s$ is the momentum transfer $s = (4\pi/\lambda) \sin \theta$, $2\theta$ is the scattering angle, $\lambda$ is the wavelength.

For a polydisperse system of interacting particles, the intensity of each component can be calculated as:

$$ I_k(s) = S_k(s) \int D_k(R) V_k(R) [\Delta \rho_k(R)]^2 i_{0k}(s, R) dR, $$

where $R$ is the size of nanoparticles, $D_k(R)$ is the normalized volume size distribution of the particles for the $k$-th component, $V_k(R)$ is the effective volume of $k$-th component, $\Delta \rho_k(R)$ is the scattering contrast of $k$-th component, $i_{0k}(s, R)$ is the normalized form factor of the $k$-th component, $S_k(s)$ is the structural factor of the $k$-th component, responsible for the interparticle interactions.

In this study we modelled the diluted solutions of the particles, therefore the effect of interparticle interference was neglected.

The program MIXTURE uses the minimization procedure due to Broyden-Fletcher-Goldfarb-Shanno (B-F-G-S) with simple bounds on the parameters. It allows one to model mixtures that contain up to ten components of different body types (spherical core-shells, cylinders, ellipsoids, dumbbells etc.). The input command file for the program MIXTURE should contain the following structural parameters, describing system: the number of components, the type of each component, the relative volume fraction of the component ($v_k$), the average size of the component ($R_k$), its polydispersity ($dR_k$) and the type of the size distribution function.

3. The ranges of stable solutions for theoretical model systems of nanoparticles

The systems under investigation contain two types of spherical nanoparticles characterized by their radii ($R_1$ and $R_2$), polydispersities ($dR_1$ and $dR_2$) and volume fractions ($v_1$ and $v_2$). Three typical cases were selected (see Table 1) for the theoretical data sets without noise (Figure 1, curve 1) and with added Gaussian and Poisson noise (Figure 1, curves 2 and 3, respectively). The relative level of the noise was equal to 25%. The corresponding volume size distributions are shown in Figure 1 (right panel). As one can see from Figure 1 the volume size distribution of the first model has two narrow separated peaks, whereas $D_k(R)$ functions of other models contain one wide and one narrow separated peaks.

| №, model number | $v_1$, relative | $v_2$, relative | $R_1$, nm | $R_2$, nm | $dR_1$, nm | $dR_2$, nm |
|-----------------|----------------|----------------|-----------|-----------|------------|------------|
| 1               | 0.25           | 0.75           | 5.0       | 15.0      | 0.1        | 0.1        |
| 2               | 0.25           | 0.75           | 5.0       | 15.0      | 2.0        | 0.1        |
| 3               | 0.25           | 0.75           | 5.0       | 15.0      | 0.1        | 4.0        |
Figure 1. The left panel contains the simulated theoretical SAS curves with the parameters from Table 1 (curve 1 - with relative noise level 0%, curve 2 - Gaussian noise 25%, curve 3 - Poisson noise 25%). The curves are vertically displaced for better visualization. The right panel displays the volume size distribution functions $D_v(R)$.

The ranges of the solution stability for each structural parameter were obtained when only one parameter was varied while the others were fixed (see Table 2). It appears that the range of stable solutions always expands in the case of Poisson noise data, whereas it becomes normally shorter in the case of Gaussian noise data (with the exception for the second model). Thus, the data with added moderate level of Poisson noise (that become closer to real experimental data) can have a wider range of convergence to the correct solution in comparison with pure (free of noise) theoretical data.

Further, for each model system the values of two parameters have been changed at the same time while the rest of the parameters were fixed. The results are shown in Figures 2-5. They display the contour plots of solution stability ranges for the following pairs of parameters: $(R_1, R_2)$ – Figure 2, $(R_1, dR_2)$ – Figure 3, $(dR_1, R_2)$ – Figure 4, $(dR_1, dR_2)$ – Figure 5. The interception of the dotted lines corresponds to the theoretical (‘true’) solution. If the restored parameters are located within 5% in the vicinity of the “true” solution, the solution is treated as successful (red areas), otherwise the solution is treated as false (blue areas).

As one can see from Figures 2-5 the dependence of the solution stability ranges is similar to the cases when only one parameter is been varied. At the same time the areas of successful solutions (red areas) depend not only on the selected pair of parameters but also on the presence of the noise in the data. They form fractal-like boundaries with separated areas of instabilities. It demonstrates a high sensitivity of the minimization method to different model parameters.
Table 2. The ranges of solution stability (only one parameter has been varied, others are fixed).

| №, model number | 1               | 2               | 3               |
|-----------------|-----------------|-----------------|-----------------|
| **Relative noise level is 0%** |                 |                 |                 |
| $dR_1$, nm      | 0.01±4.0        | 0.1±5.0         | 0.01±5.0        |
| $dR_2$, nm      | 0.01±15.0       | 0.01±15.0       | 0.2±15.0        |
| $R_1$, nm       | 3.0±6.0         | 2.1±10.0        | 2.9±6.1         |
| $R_2$, nm       | 13.8±16.2       | 14.0±16.0       | 10.0±30.0       |
| **Relative level of Gaussian noise is 25%** |                 |                 |                 |
| $dR_1$, nm      | 0.01±4.3        | 0.1±5.0         | 0.01±4.6        |
| $dR_2$, nm      | 0.2±15.0        | 0.01±18.8       | 0.2±15.0        |
| $R_1$, nm       | 3.9±6.0         | 1.0±10.0        | 3.3±6.1         |
| $R_2$, nm       | 14.0±16.0       | 14.0±16.2       | 10.0±30.0       |
| **Relative level of Poisson noise is 25%** |                 |                 |                 |
| $dR_1$, nm      | 0.01±5.0        | 0.1±6.0         | 0.01±5.0        |
| $dR_2$, nm      | 0.01±20.0       | 0.01±20.0       | 0.2±20.0        |
| $R_1$, nm       | 2.4±8.0         | 1.0±10.0        | 1.5±8.0         |
| $R_2$, nm       | 10.0±30.0       | 10.0±30.0       | 10.0±30.0       |

Figure 2. The contour plots of solution stability ranges for three model systems depending on the pair of parameters ($R_1$, $R_2$). The left column corresponds to the model 1, the central column – the model 2, the right one – the model 3. The plots for the curves without noise (relative noise level 0%) are located in the first row, with Gaussian noise (relative noise level 25%) - in the second row, with Poisson noise (relative noise level 25%) - in the third row. The interception of the dotted lines corresponds to the theoretical (‘true’) solution. If the restored parameters are located within 5% in the vicinity of ‘true’ solution, then the solution is treated as successful (red areas), otherwise the solution is treated as false (blue areas).
Figure 3. The contour plots of solution stability ranges for three model systems depending on the pair of parameters ($R_1$, $dR_2$). The notations and colours are the same as in Figure 2.

Figure 4. The contour plots of solution stability ranges for three model systems depending on the pair of parameters ($dR_1$, $R_2$). The notations and colours are the same as in Figure 2.
4. Conclusion

1) The obtained results demonstrate the possibilities for the correct model restoration and depend on the choice of the initial parameter values as well as the type and the level of the data noise.

2) It was found that the presence of Poisson noise in small-angle scattering data extends the ranges of solution stability. Thus, the addition of the moderate Poisson noise (up to 25%) to real experimental data with a high signal-to-noise ratio can increase the probability of the "true" solution.

3) In the present study the two-component system of spherical particles was considered. In future we plan to analyze the multicomponent systems of cylindrical particles as well as the mixtures of spherical and cylindrical particles.

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