

Supplementary information for

"The application of distance distribution functions to structural analysis of core-shell particles"

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Distance distribution function for a coaxial core-shell spherical particle

The electron density of the core-shell particle $\xi(r)$ can be representing as $\xi(r) = \xi_m$ for $r > R$, $\xi(r) = \xi_s$ for $R_c < r \leq R$ and $\xi(r) = \xi_c$ for $0 \leq r \leq R_c$, where R_c is a radius of the core and R is an outer radius of the shell equivalent to the total radius of the particle and ξ_c , ξ_s and ξ_m are the electron densities of the core, the shell and the surrounding medium respectively. Following the work (Glatter, 1981) the distance distribution function of a coaxial core-shell spherical particle can be expressed as

$$p_{cs}(r) = V_{cc}(r)\Delta\xi_c^2 + V_{ss}(r)\Delta\xi_s^2 + 2V_{sc}(r)\Delta\xi_s\Delta\xi_c \quad (S1)$$

where $\Delta\xi_c = \xi_m - \xi_c$ and $\Delta\xi_s = \xi_m - \xi_s$ are contrasts in electron densities between the medium and the core and between the medium and the shell, respectively; $V_{cc}(r)$, $V_{ss}(r)$ and $V_{sc}(r)$ are the overlap integrals which state the overlap of the core, the shell and the shell and the core, respectively, shifted a distance r . Taking into account the geometry factor r^2 the analytical expressions of these integrals are the following:

$$V_{cc} = \frac{1}{24}r^2\pi(r^3 - 12rR_c^2 + 16R_c^3)[1 + \text{sgn}(-r + 2R_c)], \quad (S2)$$

$$V_{ss} = \frac{1}{24}r\pi\{2r^4 - 12r^2(R_c^2 + R^2) - 16r(R_c^3 - R^3) - 2[r^4 - 6r^2(R_c^2 + R^2) - 8r(R_c^3 - R^3) - 3(R_c^2 - R^2)^2] \times \text{sgn}(r + R_c - R) - 2[r^4 - 6r^2(R_c^2 + R^2) + 8r(R_c^3 + R^3) - 3(R_c^2 - R^2)^2] \times \text{sgn}(-r + R_c + R) + (r^4 - 12r^2R_c^2 + 16rR_c^3) \times \text{sgn}(-r + 2R_c) - (r^4 - 12r^2R^2 + 16rR^3) \times \text{sgn}(r - 2R)\},$$

$$V_{sc} = -\frac{1}{24}r\pi\{r^4 - 12r^2R_c^2 - [r^4 - 6r^2(R_c^2 + R^2) - 8r(R_c^3 - R^3) - 3(R_c^2 - R^2)^2] \times \text{sgn}(r + R_c - R) - [r^4 - 6r^2(R_c^2 + R^2) + 8r(R_c^3 + R^3) - 3(R_c^2 - R^2)^2] \times \text{sgn}(-r + R_c + R) + (r^4 - 12r^2R_c^2 + 16rR_c^3) \times \text{sgn}(-r + 2R_c)\}.$$

Modelling of the distance distribution function for a system of core-shell particles with a phase separation in the shell (a model of spherical disks)

The polyurethane (PU) comprising the shell of the studied core-shell particles is spatially confined by the thickness of the shell which is comparable with the size of the hard and soft microdomains (about 150 Å) formed in phase-separated polyurethane (Hamley *et al.*, 2000). Thus, in the core-shell particles studied a spinodal decomposition wave is confined and can only propagate along the surface of the particles forming a spherical shell of phase-separated polyurethane. Following the morphology observed in the AFM images (Figure 1, b of the manuscript) it has been suggested that the PU shell in the particles can be simulated as truncated spherical cones (a geometrical figure formed by intersection of a cone and a spherical shell, for the sake of simplicity they will be called ‘spherical disks’ hereafter) corresponding to locations of the hard PU blocks and the rest of the shell surrounding the spherical disks corresponds to the soft PU (Figure 4, a of the manuscript). The spherical disks have been evenly distributed around the shell using a charge repulsion algorithm realized in the computer program ‘diffuse’ (Lettvin, 2003). A similar structural organization of phase-separated microdomains can be found in liposome membranes composed of several lipids (Baumgart *et al.*, 2003). In the results presented herein it has been assumed that hard/soft PU volume ratio, which could be controlled by both the number and the size of the spherical disks, is taken to be 1:1.

Calculations are made for both the scattered intensities $I(q)$ and the distance distribution functions of the model of spherical disks. There is unique connection between these two functions given by a Fourier transformation:

$$p(r) = \int_0^{\infty} I(q)qr \sin(qr) dq \quad (S3)$$

The distance distribution function for the system of core-shell particles with a phase-separated polymer in the shell cannot be analytically expressed; therefore, numerical methods have been applied for the calculations. To calculate the distance distribution function for the model particles surrounded by a medium with a variable electron density an ensemble of one hundred particles have been generated for each case using the charge repulsion algorithm for positioning the spherical disks and a Monte Carlo algorithm for random orientation of the particles in space. Thus, the resultant $p(r)$ was obtained as:

$$p(r) = 1/N \sum_{j=1}^N p_j(r) \quad (S4)$$

where N is the number of particles and the index j corresponds to the j^{th} particle in the generated ensemble. It has to be noted that even the spherical disks have been distributed evenly their relative positions can still be random and may break a symmetry of the core-shell particles (however, some certain numbers of disks, for example 4 or 8, form unique symmetrical configurations). Therefore, the general formula for the scattering amplitude has been used in the calculations:

$$F(\vec{q}) = \int_V \xi(\vec{r}) e^{-i\vec{q}\vec{r}} d\vec{r} \quad (\text{S5})$$

where the integration is carried out over the volume of the particle V and $\xi(\vec{r})$ denotes electron density variations in the particle. It is more convenient to describe the structure of the particles in spherical coordinates and to use the corresponding formula for the scattering amplitude (Roe, 2000):

$$F_j(q) = (\xi_c - \xi_m) R_c^3 f(qR_c) + \int_0^{2\pi} \int_0^R \int_{R_c}^R [\xi_s^j(R_{sp}, \theta, \varphi) - \xi_m] e^{-i2\pi q R_{sp} \cos \theta} R_{sp}^2 \sin \theta dR_{sp} d\theta d\varphi \quad (\text{S6})$$

where the first term represents amplitude of scattering from the core, the integral part corresponds to the scattering from the shell, $\xi_s^j(R_{sp}, \theta, \varphi)$ describes the electron density distribution in the shell of the j^{th} particle and R_{sp}, θ, φ are spherical coordinates. The spatially averaged intensity of scattering from the particle, which could be measured from SAXS experiments, is expressed as the absolute square of the amplitude of scattering from equation (S6) using the conjugate complex $F^*(\vec{q})$:

$$I(q) = \langle |F(\vec{q})|^2 \rangle = \langle F(\vec{q}) F^*(\vec{q}) \rangle \quad (\text{S7})$$

where extra coefficients corresponding to geometry of the experiments, the intensity of the X-ray beam, the irradiated volume of the sample and electron's scattering should be added to interpret a real pattern of intensity of scattering obtained from SAXS measurements. The scattering amplitudes $F_j(q)$ and corresponding $p_j(r)$ have been calculated by a numerical integration equation (S6) and equation (S3), respectively.

Two conditions have been considered in the calculations: firstly, the condition where the electron densities of the hard and soft blocks of PU are slightly different (0.012 electrons/Å³, model 1) and the mass densities are 1.12 g/cm³ (hard block) and 1.08 g/cm³ (soft block), or secondly, where the electron densities are significantly different (0.06 electrons/Å³, model 2) and in this scenario the mass densities are 1.2 g/cm³ and 1.0 g/cm³. The results obtained have shown that in aqueous medium the $p(r)$ for both models virtually matched the $p(r)$ of the typical core-shell structure (Figure 4, b in the manuscript). Noticeable deviations from the core-shell $p_{cs}(r)$ have been found only for the model 2, which demonstrates strong oscillations in the distance distribution functions corresponding to the model particles surrounded by the media with electron density between the average electron density of the shell $\langle \xi_s \rangle$ (0.364 electrons/Å³, mass density of the water sucrose solution 1.10 g/cm³) and the ξ_c (0.379 electrons/Å³, mass density of the water sucrose solution 1.15 g/cm³), see Figure 4, c and d. The appearance of the peaks in these oscillations can be qualitatively interpreted as the distance distribution function of the spherical disks themselves (the first peak) and as the correlation distances between the nearest neighbouring disks and the next nearest neighbouring disks. The

smaller diameter and greater number of disks at a given particle size the more oscillations would appear in $p(r)$.

To model a random distribution of the spherical disks in the shell (instead of the even distribution used above), a Monte Carlo algorithm has been applied, producing a similar result but with less pronounced oscillations and smoothed peak in the distance distribution function patterns. Imposition of polydispersity in the radii of the spherical disks led to a further degradation of the patterns into the patterns corresponding to a standard core-shell particle in which the electron density of the shell could be either a constant or a result of electron density averaged over a stochastic distribution of the hard and the soft blocks of PU material.

The simulations presented have shown that only well-defined phase separation in the shell structure with significant difference in the electron densities of the phase-separated materials can be detected from SAXS measurements. Some oscillations, which may occur from a phase-separated PU in the shell, can be identified in the distance distribution functions obtained for latex particles diluted in the contrast sucrose solutions with ρ_m in a range between 1.10 g/cm³ and 1.16 g/cm³ (Figure 3, left-hand side, in the manuscript). However, these oscillations are mostly within the error limits of the distance distribution function calculations. Furthermore, taking into account the criterion chosen for the best solution of the distance distribution function using regularization method (maximal TOTAL parameter), where the OSCILL parameter is not properly defined for a particular structure (Svergun, 1992), the obtained SAXS results do not allow a definitive conclusion to be reached about the precise nature of the phase-separation in the PU material in the core-shell latex particles. The simulations suggest that if there is a phase-separation of the polyurethane in the shell of the particles then either the difference between electron densities of the hard block domains and the soft block domains should be in a region 0.01-0.02 electrons/Å³ and/or the ordering of phase-separated domains is not well defined in the shell of the particles producing stochastic distribution of the phase-separated PU material.

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