Supplementary Material for
"Form factor of cylindrical superstructures composed of globular particles"

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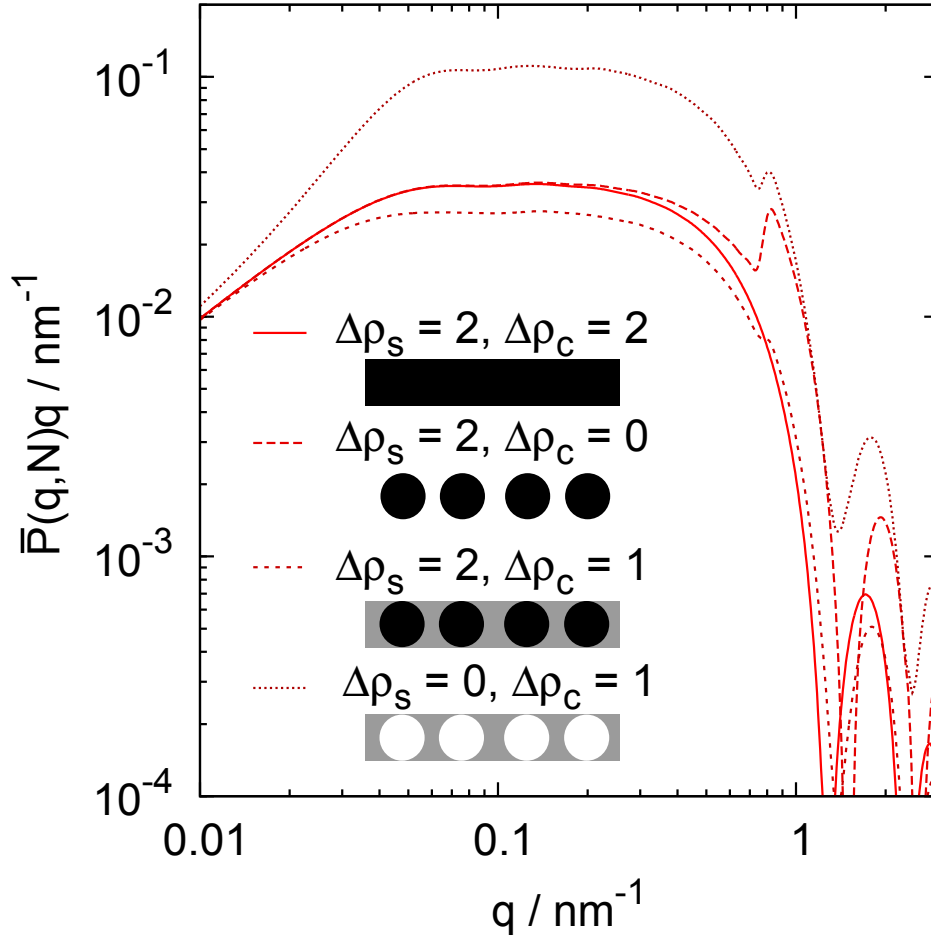
Figure S1: $\overline{P}(q)q$ from objects made up of ten spheres of radius 3 nm, with $D = 8$ nm included in a cylinder with radius of 3 nm and length $L = N \cdot D = 80$ nm, are reported as a function of the scattering vector. Scattering contrasts are in arbitrary units. A schematic representation of the objects is given in the inset.

Radii of gyration

The radius of gyration is defined as follows:

$$R_g^2 = \frac{\int_V \vec{r}^2 \rho(\vec{r}) \mathrm{d}\vec{r}}{\int_V \rho(\vec{r}) \mathrm{d}\vec{r}} \tag{S1}$$

where $\rho(\vec{r})$ describes the scattering length density in space. The case of the sphere is usually solved in spherical coordinates. The problem of a series of spheres on a row was already analyzed by Kawaguchi and it was found that it is more convenient to solve the integral in cylindrical coordinates rather than in spherical ones. In detail, looking at a sphere located at a z-coordinate d, the following expression is obtained (Kawaguchi, 2001):

$$R_g^2 = \frac{\int_0^{2\pi} \mathrm{d}\phi \int_{d-R}^{d+R} \mathrm{d}z \int_0^{\alpha} (r^2 + z^2) r \mathrm{d}r}{4\pi R^3/3} \tag{S2}$$

with $\alpha = \sqrt{R^2 - (z-d)^2}$. In the case of a sphere with radius R located at a distance D from the center of rotation, the radius of gyration is given by(Kawaguchi, 2001):

$$R_g^2 = \frac{4\pi R^5/5 + 4\pi R^3 D^2/3}{4\pi R^3/3} = \frac{3}{5} R^2 + D^2 \tag{S3}$$

when we consider N spheres, each center spaced by a distance D and each being at a distance d_j from the center of mass of the object

$$d_j = \left(j - \frac{N-1}{2} \right) D \tag{S4}$$

with $j = 0, 1, 2, \ldots, N-1$, the following relation is obtained:

$$R_g^2 = \frac{\sum_{j=0}^{N-1} 4\pi R^5/5 + \sum_{j=0}^{N-1} 4\pi R^3 d_j^2/3}{\sum_{j=0}^{N-1} 4\pi R^3/3} = \frac{3}{5} R^2 + \frac{\sum_{j=1}^{N} d_j^2}{N} \tag{S5}$$

with

$$\sum_{j=0}^{N-1} d_j^2 = \frac{N^3 - N}{12} D^2 \tag{S6}$$

resulting in

$$R_g^2 = \frac{3}{5} R^2 + \frac{N^2 - 1}{12} D^2 \tag{S7}$$

When the particles are in contact (i.e. $D = 2R$) the expression simplifies into

$$R_g^2 = R^2 \left[\frac{3}{5} + \frac{1}{3}(N^2 - 1) \right] \tag{S8}$$

In the case of aligned rotational ellipsoids, Eq. S2, has to be rewritten accordingly:

$$R_g^2 = \frac{\int_0^{2\pi} d\phi \int_{d-A}^{d+A} dz \int_0^{\alpha} (r^2 - z^2) r dr}{4\pi A B^2/3} \tag{S9}$$

with $\alpha = \sqrt{B^2 - (z-d)^2}$. A is the rotational semi-axis and B the equatorial semi-axis.

When an object made up of N aligned spheres of radius R spaced by a distance D inside a cylinder of radius R and length L is considered, the radius of gyration is given by:

$$R_g^2 = \frac{\rho_{cyl}(\int_{V_{cyl}} \vec{r}^2 d\vec{r} - \int_{V_{Nob}} \vec{r}^2 d\vec{r}) + \rho_{ob} \int_{V_{Nob}} \vec{r}^2 d\vec{r}}{\rho_{ob} V_{Nob} + \rho_{cyl}(V_{cyl} - V_{Nob})} \tag{S10}$$

where V_{cyl} and V_{Nob} are the volume of the whole cylinder and that of the N objects. $\int_{V_{cyl}}$ and $\int_{V_{Nob}}$ are the integrals over the volumes of the whole cylinder and the N objects. The solution of this expression is shown after and the final expression is:

$$R_g^2 = \frac{\frac{12}{5}\Delta\rho N R^3 - \frac{3}{2}(\Delta\rho + \rho_{ob})LR^2 + \frac{1}{3}\Delta\rho D^2 R N(N^2 - 1) - \frac{1}{4}(\Delta\rho + \rho_{ob})L^3}{4\Delta\rho N R - 3L(\Delta\rho + \rho_{ob})} \tag{S11}$$

with $\Delta\rho = \rho_{cyl} - \rho_{ob}$. It can be easily shown that Eq. S11 returns the R_g of a cylinder if $\rho_{ob} = \rho_{cyl}$ and that of N aligned spheres if $\rho_{cyl} = 0$.

The radius of gyration of N aligned spheres of radius R spaced by a distance D inside a cylinder of radius R and length L is defined in Eq. S10, with:

$$\int_{V_{cyl}} \vec{r}^2 d\vec{r} = \int_0^{2\pi} d\phi \int_{-L/2}^{L/2} dz \int_0^R (r^2 + z^2) r dr = \frac{\pi}{12}\left(6LR^4 + L^3 R^2\right) \tag{S12a}$$

$$\int_{V_{Nob}} \vec{r}^2 d\vec{r} = \sum_i \int_0^{2\pi} d\phi \int_{D-R}^{D+R} dz \int_0^{\alpha} (r^2 + z^2) r dr = \frac{4}{5}N\pi R^5 + \frac{1}{9}\pi R^3 N(N^2 - 1)D^2 \tag{S12b}$$

$$\int_{V_{cyl}} d\vec{r} = \int_0^{2\pi} d\phi \int_{-L/2}^{L/2} dz \int_0^R r dr = \pi R L^2 \tag{S12c}$$

$$\int_{V_{Nob}} d\vec{r} = \sum_i \int_0^{2\pi} d\phi \int_{D-R}^{D+R} dz \int_0^{\alpha} r dr = \frac{4}{3}\pi N R^3 \tag{S12d}$$

Experimental details

Low molecular weight chitosan was obtained from TCI Europe and purified according to Sorlier *et al.* (Sorlier *et al.*, 2001). Nonaoxyethylene oleylether carboxylic acid is a technical surfactant obtained from the Kao Chemical Company and was used without purification. Samples were prepared in 0.2 M Acetic acid /Acetate buffer solution at pH = 4.0 in heavy water (Eurositop, 99% D content), with constant chitosan concentration of 0.3 % in mass. Small angle neutron scattering (SANS) curves were

recorded at D11 at the Institut Laue-Langevin, Grenoble, France. Three different configurations were used, with a wavelength of $\lambda = 6.0$ Å and full width at half maximum (fwhm) of 10 %, sample-to-detector distances of 1.2, 8 and 34 m and collimation of 4, 8 and 34 m, respectively, covering a q-range of 0.02 - 3 nm^{-1}. However, here only the mid-q and high-q part are discussed. For the complete curves and further experimental details please refer to our recent work (Chiappisi *et al.*, 2014).

Scattering from RO90 micelles

The scattering form factor of a core-shell rotational ellipsoid is given by (Bendedouch & Chen, 1984):

$$P(q) = \int_0^1 |F(q, \cos\alpha)| \mathrm{d}\cos\alpha \tag{S13}$$

with α being the angle formed by the scattering vector and the rotational axis of the ellipsoid. $F(q, \cos\alpha)$ is the scattering amplitude and is given by

$$F(q, \cos\alpha) = (\mathrm{SLD_c} - \mathrm{SLD_{sh}})\, V_c \left[\frac{3j_1(x_c)}{x_c} \right] + (\mathrm{SLD_{sh}} - \mathrm{SLD_{sol}})\, V_t \left[\frac{3j_1(x_t)}{x_t} \right] \tag{S14}$$

with $j_1(x)$ being the first order spherical Bessel function:

$$j_1(x) = \frac{\sin(x) - x\cos(x)}{x^2} \tag{S15}$$

x_c and x_t are given by:

$$x_c = q\sqrt{a^2 \cos\alpha^2 + b^2(1 - \cos\alpha^2)} \tag{S16}$$

$$x_t = q\sqrt{(a+t)^2 \cos\alpha^2 + (b+t)^2(1 - \cos\alpha^2)} \tag{S17}$$

and the volumes of the core and of the particle are

$$V_c = \frac{4}{3}\pi a b^2 \tag{S18}$$

$$V_t = \frac{4}{3}\pi (a+t)(b+t)^2 \tag{S19}$$

$\mathrm{SLD_c}$, $\mathrm{SLD_{sh}}$, and $\mathrm{SLD_{sol}}$ are the scattering length densities of the core, shell and of the medium (D$_2$O).

Scattering from free chitosan chains

The scattering arising from chitosan can be described with a generalized gaussian chain model (Flory, 1969):

$$I(q) = I(0)_{chi} \frac{U^{-2\nu} \left[\Gamma\left(\frac{1}{2\nu}, 0\right) - \Gamma\left(\frac{1}{2\nu}, U\right) \right] - \Gamma\left(\frac{1}{\nu}, 0\right) + \Gamma\left(\frac{1}{\nu}, U\right)}{\nu U^{-\nu}} \tag{S20}$$

with

$$U = (2\nu + 1)(2\nu + 2)\frac{q^2 Rg^2}{6} \tag{S21}$$

and

$$\Gamma(a, x) = \int_x^\infty t^{a-1} \exp(-t)\, \mathrm{d}t \tag{S22}$$

with $I(0)_{chi}$ and R_g being the forward scattering intensity and the radius of gyration of the polymer chain, respectively. ν is the excluded volume parameter.

References

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