Supporting information

Mass-fractal growth in niobia/silsesquioxane mixtures: A SAXS study

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1. Mass-fractal agglomerates with an exponential cut-off length $\xi$

The diffusion limited cluster aggregation (DLCA) mechanism typically leads to less polydisperse agglomerates, as implied by the exponentially decaying cut-off function (Sorensen & Wang, 1999). Sharper cut-off functions such as a Gaussian cutoff $h(r, \xi) = \exp(-r^2/\xi^2)$ are realistic for a variety of aggregation mechanisms. It would be convenient to define a function of which the cutoff behavior can be related to the degree of polydispersity. To this end, firstly we introduce an infinitely sharp cut-off function, i.e. a unit step or Heaviside step function $h(r, \xi) = H(\xi - r)$. The intensity function of a mass fractal with a hard cutoff function was described by a rotationally averaged Fourier transform:

\[
S_{HC}(q, \xi) = \frac{4\pi}{q \cdot V_A} \int_0^\infty H(\xi - r) \cdot r^{D_1 - 2} \cdot \sin(q \cdot r) dr = \frac{4\pi}{q \cdot V_A} \int_0^\xi r^{D_1 - 2} \cdot \sin(q \cdot r) dr 
\]  

(S1)

Herein, $H(\xi - r) = 1$ for $r < \xi$ and $H(\xi - r) = 0$ for $r > \xi$. Since the volume or primary units was assumed infinite small $S(q)$ was being normalized over its entire agglomerate volume $V_A$.

Instead of using the unit step function we can also move the upper boundary of the sine transform from $\infty$ to $\xi$, as shown in the right hand side part of Equation (S1). Secondly, polydispersity is introduced by the integral:
Herein, \( w(\xi) \) is an intensity weighted probability density function of the cutoff parameter \( \xi \).

We applied a Schultz-Zimm distribution (Kotlarchyk & Chen, 1983), which was found to give realistic results in earlier studies on similar systems (Besselink et al., 2013; Stawski et al., 2011a,b; Pontoni et al., 2002):

\[
S_{SC}(q, \xi) = \int_{0}^{\infty} w(\xi) \cdot S_{HC}(q, \xi) d\xi
\]

(S2)

This integral can be evaluated as a Laplace transform and for integer values of \( Z \).

An analytical solution is given by

\[
S_{SC}(q, a, D, Z) = \frac{4\pi \cdot a^{Z+1}}{q \cdot V \cdot \Gamma(Z+1)} \cdot \left[ \xi^{Z} \left( \int_{0}^{\xi} r^{D-2} \cdot \sin(q \cdot r) dr \right) \cdot \exp(-a \cdot \xi) \right] d\xi
\]

(S4)

where \( a = \frac{Z + 1}{\mu} \)

and \( \mu \) is the intensity weighted average of \( \xi \) and the \( Z \)-parameter is related to the distribution of the cutoff distance, i.e., the variance of \( \xi \) corresponds to \( \sigma_{\xi}^2 = \frac{\mu^2}{Z+1} \). By combining Equation (S1)-(S3) we obtain:

\[
S_{SC}(q, a, D, Z) = \frac{4\pi \cdot a^{Z+1}}{q \cdot V \cdot \Gamma(Z+1)} \cdot \left[ \xi^{Z} \left( \int_{0}^{\xi} r^{D-2} \cdot \sin(q \cdot r) dr \right) \cdot \exp(-a \cdot \xi) \right] d\xi
\]

(S4)

This integral can be evaluated as a Laplace transform and for integer values of \( Z \). An analytical solution is given by

\[
S_{SC}(q, a, D, \zeta) = \frac{4\pi \cdot a^{Z+1}}{2i \cdot q \cdot V \cdot \Gamma(Z+1)} \cdot (-1)^{Z} \cdot \frac{d^Z}{da^Z} \left( \frac{1}{a} \cdot \left( \frac{1}{(a - i \cdot q)^{D-1}} - \frac{1}{(a + i \cdot q)^{D-1}} \right) \right)
\]

(S5)

where \( i \) is the imaginary number. The derivatives of \( a \) that are expanding with increasing \( Z \) can be generalized by the following Riemann's sum:
Here, $\eta$ is an integer variable that varies from 0 to $Z$. In analogy with the mass fractal structure function with an exponential cutoff Equation (S2), the function is normalized over its agglomerate volume $V_A$ such that $S(q\rightarrow0) = 1$. The Porod volume of such agglomerate is described by:

$$
V_A = 4\pi \left( \frac{a^{Z+1}}{\Gamma(Z+1)} \right) \int_0^\infty \xi^Z \left( \int_0^\xi r^{D_f-3} r^2 dr \right) \exp(-a\cdot\xi) d\xi
$$

which corresponds to:

$$
V_A = \frac{4\pi \cdot \Gamma(D_f + Z + 1)}{D_f \cdot \Gamma(Z+1)} \left( \frac{\mu}{Z + 1} \right)^{D_f}
$$

Then, after normalization of Equation (S6) with Equation (S8), and replacing complex elements with goniometric equations we obtain:

$$
S_{SC}(q, a, D_f, \xi) = \frac{4\pi}{2i \cdot q \cdot V_p} \sum_{\eta=0}^Z \left( \frac{\Gamma(D_f + \eta - 1)}{\Gamma(\eta + 1)} \cdot a^\eta \cdot \left( \frac{1}{(a - i \cdot q)^{D_f+\eta-1}} - \frac{1}{(a + i \cdot q)^{D_f+\eta-1}} \right) \right)
$$

(S6)

Now, let us define $\zeta$ as the integer part of $Z$ and $\phi$ as the fractional part of $Z$. Subsequently, we may approximate the structure function including fractional values as a linear combination of $S(\zeta)$ and $S(\zeta+1)$, i.e. $S(q) = (1-\phi) \cdot S(\zeta) + \phi \cdot S(\zeta+1)$. Since $S(\zeta+1) = S(\zeta) + S_f(\zeta+1)$, where $S_f(\zeta+1)$ only contains the $\zeta+1$ component of the Riemann's sum, this can be simplified to:

$$
S_{SC}(q, a, D_f, Z) = \frac{a}{q} \cdot \frac{D_f \cdot \Gamma(Z+1)}{\Gamma(D_f + Z + 1)} \sum_{\eta=0}^Z \left( \frac{\Gamma(D_f + \eta - 1)}{\Gamma(\eta + 1)} \cdot \frac{\sin\left(\left(\frac{D_f + \eta - 1}{2}\right) \cdot \arctan\left(\frac{q}{a}\right)\right)}{1 + \left(\frac{q}{a}\right)^2} \right)
$$

(S9)
\[ S_{SC}(q, \mu, D_f, Z) = \frac{D_f \cdot \Gamma(Z+2)}{(q \cdot \mu) \cdot \Gamma(D_f + Z + 1)} \cdot \left( S_I + \phi \cdot S_F \right) \] (S10)

where:

\[
S_I = \sum_{\eta=0}^{\zeta} \frac{\Gamma(D_f + \eta - 1)}{\Gamma(\eta + 1)} \cdot \sin \left( \frac{(D_f + \eta - 1) \cdot \text{atan} \left( \frac{q \cdot \mu}{Z+1} \right)}{2} \right) \cdot \left( 1 + \left( \frac{q \cdot \mu}{Z+1} \right)^2 \right)^{\left( \frac{(D_f + \eta - 1)}{2} \right)}
\]

and:

\[
S_F = \frac{\Gamma(D_f + \zeta)}{\Gamma(\zeta + 2)} \cdot \sin \left( \frac{(D_f + \zeta) \cdot \text{atan} \left( \frac{q \cdot \mu}{Z+1} \right)}{2} \right) \cdot \left( 1 + \left( \frac{q \cdot \mu}{Z+1} \right)^2 \right)^{\left( \frac{(D_f + \zeta)}{2} \right)}
\]

\[ \zeta = \text{floor} (Z) \quad \text{and} \quad \phi = Z - \zeta. \]

Here \( S_I \) and \( S_F \) represent the contributions of the integer and fractional values of \( Z \) to \( S_{SC}(q) \).

\[ I(q) = I_0 \cdot S(q) \] (S11)

where \( I_0 = N \cdot (V_A)^2 \cdot (\Delta \rho)^2 \), which corresponds to the scattering intensity at \( q \to 0 \) (since \( S(q \to 0) = 1 \)), \( N \) is the particle number density, \( V_A \) the particle volume of the fractal agglomerate (Equation (S8)) and \( \Delta \rho \) and is the averaged difference in electron density between particles and their surroundings. For comparison of the Schultz cut-off model with the exponential cutoff model it is more convenient to express the size of a cluster by the radius of gyration that is derived from Feigin & Svergun (1987) and Porod (1982):
\[
(R_G)^2 = \frac{1}{2} \frac{\int_0^\infty r^4 \cdot \gamma(r) dr}{\int_0^\infty r^2 \cdot \gamma(r) dr}
\]

which corresponds to:

\[
(R_G)^2 = \frac{1}{2} \frac{\int_0^\infty \xi z \left( \int_0^\xi r^4 \cdot r^{D_\gamma - 3} dr \right) \cdot \exp(-a \cdot \xi) d\xi}{\int_0^\infty \xi z \left( \int_0^\xi r^2 \cdot r^{D_\gamma - 3} dr \right) \cdot \exp(-a \cdot \xi) d\xi}
\]

The solution is

\[
R_G = \left( \frac{\mu}{Z + 1} \right) \left[ \frac{1}{2} \frac{D_\gamma \cdot (D_\gamma + Z + 1) \cdot (D_\gamma + Z + 2)}{(D_\gamma + 2)} \right]
\]

Since \( \gamma(r) \) is essentially an auto-convolution product of \( \Delta \rho(r) \) a hard cutoff function is not realistic. The relative variance of \( \xi \) that can be derived from the \( Z \) parameter is always larger, because the relative variance of \( R_G \) and the relationship between \( Z \) and polydispersity depends on the geometry of the fractal. Alternatively, we may extract a polydispersity factor \( C_P \) following the procedure described by Sorensen and Wang (1999). Provided that \( S(q) \) is normalized over the entire agglomerate volume Equation (S8), such that \( S(q \to 0) = 1 \), the effective structure function in the fractal regime \( (q \cdot R_G \gg 1) \) is described by:

\[
S_{\text{eff}}(q, R_G) = C \cdot C_P \cdot (q \cdot R_G)^{-D_\gamma} \quad \text{for:} \quad q \cdot R_G \gg 1
\]

where the constant \( C \) is related to the geometry of the fractalic agglomerate and \( C_P \) is a measure of the polydispersity (Sorensen and Wang, 1999). Experimental data revealed that \( C = 1.0 \pm 0.05 \) for mass fractals with \( D_\gamma \) between 1.7 and 2.1 (Sorensen and Wang, 1999).
The $C_p$ value increases with increasing polydispersity and can be associated with a particular growth mode, i.e. $C_p \sim 1.5$ for diffusion limited cluster aggregation (DLCA) and $C_p > 2$ for reaction limited cluster aggregation (RLCA) (Sorensen and Wang, 1999). $C_p$ is a size independent measure of polydispersity and depends solely on $Z$ and $D_f$. It can be derived from Equation (S9) by taking the limit $(q \cdot R_G) \to \infty$ of $S_{SC}(q \cdot R_G) \cdot (q \cdot R_G)^D$, which corresponds to:

$$C \cdot C_p = \sin \left( \frac{(D_f - 1) \pi}{2} \right) \cdot \left( \frac{D_f \cdot \Gamma(D_f - 1) \cdot \Gamma(Z + 1)}{\Gamma(D_f + Z + 1)} \right) \cdot \left( \frac{1}{2} \cdot \frac{D_f \cdot (D_f + Z + 1) \cdot (D_f + Z + 2)}{(D_f + 2)} \right)^{\frac{D_f}{2}}$$

(S16)

Note that the Riemann's sum diminished since the limit was dominated by the $\eta = 0$ element of the Riemann's sum. As illustrated in Figure 2 by simulations of $S_{SC}(q, \mu, D_f, Z)$ with $R_G = 10$ nm and $D_f = 2$, the height of the fractal regime as characterized by $C \cdot C_p$ decreases with increasing $Z$ value.

2. References

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