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 ξ

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(-($r/\xi)^2$) 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:

$$S_{\mathrm{HC}}(q,\xi)=\frac{4\pi}{q\cdot V_{\mathrm{A}}}\int_0^{\infty} H(\xi-r)\cdot r^{D_{\mathrm{f}}-2}\cdot\sin(q\cdot r)dr=\frac{4\pi}{q\cdot V_{\mathrm{A}}}\int_0^{\xi} r^{D_{\mathrm{f}}-2}\cdot\sin(q\cdot r)dr \qquad \text{(S1)}$$

Herein, $H(\xi-r) = 1$ for $r < \xi$ and $H(\xi-r) = 0$ for r > ξ. 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 ∞ to ξ, as shown in the right hand side part of Equation (S1). Secondly, polydispersity is introduced by the integral:

$$S_{\mathrm{SC}}(q,\xi) = \int_0^\infty w(\xi)\cdot S_{\mathrm{HC}}(q,\xi)d\xi \tag{S2}$$

Herein, $w(\xi)$ is an intensity weighted probability density function of the cutoff parameter ξ. 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):

$$w(\xi,\mu,z) = \frac{a^{Z+1}}{\Gamma(Z+1)}\cdot\xi^{Z}\cdot\exp(-a\cdot\xi) \tag{S3}$$

where

$$a = \frac{Z+1}{\mu}$$

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

$$S_{\mathrm{SC}}(q,a,D_{\mathrm{f}},Z) = \frac{4\pi\cdot a^{Z+1}}{q\cdot V_{\mathrm{P}}\cdot\Gamma(Z+1)}\cdot\int_0^\infty\left[\xi^{Z}\left(\int_0^\xi r^{D_{\mathrm{f}}-2}\cdot\sin(q\cdot r)dr\right)\cdot\exp(-a\cdot\xi)\right]d\xi \tag{S4}$$

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

$$S_{\mathrm{SC}}(q,a,D_{\mathrm{f}},\zeta) = \frac{4\pi\cdot a^{Z+1}}{2\mathrm{i}\cdot q\cdot V_{\mathrm{P}}\cdot\Gamma(Z+1)}\cdot(-1)^{Z}\cdot\frac{d^{Z}}{da^{Z}}\left(\frac{1}{a}\cdot\left(\frac{1}{(a-\mathrm{i}\cdot q)^{D-1}}-\frac{1}{(a+\mathrm{i}\cdot q)^{D-1}}\right)\right) \tag{S5}$$

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:

$$S_{\mathrm{SC}}(q,a,D_{\mathrm{f}},\zeta)=\frac{4\pi}{2\mathrm{i}\cdot q\cdot V_{\mathrm{P}}}\cdot\sum_{\eta=0}^{Z}\left(\frac{\Gamma(D_{\mathrm{f}}+\eta-1)}{\Gamma(\eta+1)}\cdot a^{\eta}\cdot\left(\frac{1}{(a-\mathrm{i}\cdot q)^{D_{\mathrm{f}}+\eta-1}}-\frac{1}{(a+\mathrm{i}\cdot q)^{D_{\mathrm{f}}+\eta-1}}\right)\right) \quad \text{(S6)}$$

Here, η 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 $S(q\rightarrow 0) = 1$. The Porod volume of such agglomerate is described by:

$$V_{\mathrm{A}}=4\pi\cdot\left(\frac{a^{Z+1}}{\Gamma(Z+1)}\right)\cdot\int_{0}^{\infty}\xi^{Z}\left(\int_{0}^{\xi}r^{D_{\mathrm{f}}-3}\cdot r^{2}dr\right)\cdot\exp(-a\cdot\xi)d\xi \quad \text{(S7)}$$

which corresponds to:

$$V_{\mathrm{A}}=\frac{4\pi\cdot\Gamma(D_{\mathrm{f}}+Z+1)}{D_{\mathrm{f}}\cdot\Gamma(Z+1)}\cdot\left(\frac{\mu}{Z+1}\right)^{D_{\mathrm{f}}} \quad \text{(S8)}$$

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

$$S_{\mathrm{SC}}(q,a,D_{\mathrm{f}},Z)=\left(\frac{a}{q}\right)\cdot\frac{D_{\mathrm{f}}\cdot\Gamma(Z+1)}{\Gamma(D_{\mathrm{f}}+Z+1)}\cdot\sum_{\eta=0}^{Z}\left(\frac{\Gamma(D_{\mathrm{f}}+\eta-1)}{\Gamma(\eta+1)}\cdot\frac{\sin\left((D_{\mathrm{f}}+\eta-1)\cdot\mathrm{atan}\left(\frac{q}{a}\right)\right)}{\left(1+\left(\frac{q}{a}\right)^{2}\right)^{\left(\frac{(D_{\mathrm{f}}+\eta-1)}{2}\right)}}\right) \quad \text{(S9)}$$

Now, let us define ζ as the integer part of Z and ϕ 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 $S(\zeta+1) = S(\zeta) + S_{\mathrm{F}}(\zeta+1)$, where $S_{\mathrm{F}}(\zeta+1)$ only contains the $\zeta+1$ component of the Riemann's sum, this can be simplified to:

$$S_{\mathrm{SC}}(q,\mu,D_{\mathrm{f}},Z)=\frac{D_{\mathrm{f}}\cdot\Gamma(Z+2)}{(q\cdot\mu)\cdot\Gamma(D_{\mathrm{f}}+Z+1)}\cdot\left(S_{\mathrm{I}}+\phi\cdot S_{\mathrm{F}}\right) \tag{S10}$$

where:

$$S_{\mathrm{I}}=\sum_{\eta=0}^{\zeta}\left(\frac{\Gamma(D_{\mathrm{f}}+\eta-1)}{\Gamma(\eta+1)}\cdot\frac{\sin\left(\left(D_{\mathrm{f}}+\eta-1\right)\cdot\operatorname{atan}\left(\frac{q\cdot\mu}{Z+1}\right)\right)}{\left(1+\left(\frac{q\cdot\mu}{Z+1}\right)^{2}\right)^{\left(\frac{(D_{\mathrm{f}}+\eta-1)}{2}\right)}}\right)$$

and:

$$S_{\mathrm{F}}=\frac{\Gamma(D_{\mathrm{f}}+\zeta)}{\Gamma(\zeta+2)}\cdot\frac{\sin\left(\left(D_{\mathrm{f}}+\zeta\right)\cdot\operatorname{atan}\left(\frac{q\cdot\mu}{Z+1}\right)\right)}{\left(1+\left(\frac{q\cdot\mu}{Z+1}\right)^{2}\right)^{\left(\frac{(D_{\mathrm{f}}+\zeta)}{2}\right)}},$$

ζ = floor (Z) and $\phi = Z - \zeta$.

Here S_{I} and S_{F} represent the contributions of the integer and fractional values of Z to $S_{\mathrm{SC}}(q)$.

$$I(q)=I_0\cdot S(q) \tag{S11}$$

where $I_0 = N\cdot(V_A)^2\cdot(\Delta\rho)^2$, which corresponds to the scattering intensity at $q\rightarrow 0$ (since $S(q\rightarrow 0) = 1$), N is the particle number density, V_A the particle volume of the fractalic 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):

$$(R_{\mathrm{G}})^2 = \frac{1}{2}\cdot\frac{\int_0^\infty r^4\cdot\gamma(r)dr}{\int_0^\infty r^2\cdot\gamma(r)dr} \tag{S12}$$

which corresponds to:

$$(R_{\mathrm{G}})^2 = \frac{1}{2}\cdot\frac{\int_0^\infty \xi^z\left(\int_0^\xi r^4\cdot r^{D_{\mathrm{f}}-3}dr\right)\cdot\exp(-a\cdot\xi)d\xi}{\int_0^\infty \xi^z\left(\int_0^\xi r^2\cdot r^{D_{\mathrm{f}}-3}dr\right)\cdot\exp(-a\cdot\xi)d\xi} \tag{S13}$$

The solution is

$$R_{\mathrm{G}} = \left(\frac{\mu}{Z+1}\right)\cdot\sqrt{\frac{1}{2}\cdot\frac{D_{\mathrm{f}}\cdot(D_{\mathrm{f}}+Z+1)\cdot(D_{\mathrm{f}}+Z+2)}{(D_{\mathrm{f}}+2)}} \tag{S14}$$

Since $\gamma(r)$ is essentially an auto-convolution product of $\Delta\rho(r)$ a hard cutoff function is not realistic. The relative variance of ξ 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 $S(q\rightarrow 0)$ =1), the effective structure function in the fractal regime ($q\cdot R_{\mathrm{G}}$ >> 1) is described by:

$$S_{\mathrm{eff}}(q, R_{\mathrm{G}}) = C\cdot C_{\mathrm{P}}\cdot(q\cdot R_{\mathrm{G}})^{-D_{\mathrm{f}}} \quad \text{for:} \quad q\cdot R_{\mathrm{G}} >> 1 \tag{S15}$$

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 ± 0.05 for mass fractals with D_{f} 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~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 $(q \cdot R_G) \rightarrow \infty$ of $S_{SC}(q \cdot R_G) \cdot (q \cdot R_G)^{D_f}$, which corresponds to:

$$C \cdot C_P = \sin\left[(D_f - 1) \cdot \frac{\pi}{2}\right] \cdot \left(\frac{D_f \cdot \Gamma(D_f - 1) \cdot \Gamma(Z+1)}{\Gamma(D_f + Z + 1)}\right) \cdot \left(\frac{1}{2} \cdot \frac{D_f \cdot (D_f + Z + 1) \cdot (D_f + Z + 2)}{(D_f + 2)}\right)^{\left(\frac{D_f}{2}\right)} \quad \text{(S16)}$$

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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