Limits of the Guinier method for the analysis of polydisperse scattering patterns.

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In small-angle scattering, an ofttimes used tool for small-angle scattering pattern analysis is the "Guinier method". This method revolves around the analysis of the initial scattering behaviour of centrosymmetric, rotationally averaged (isotropic) particles, for which the intensity is described as:

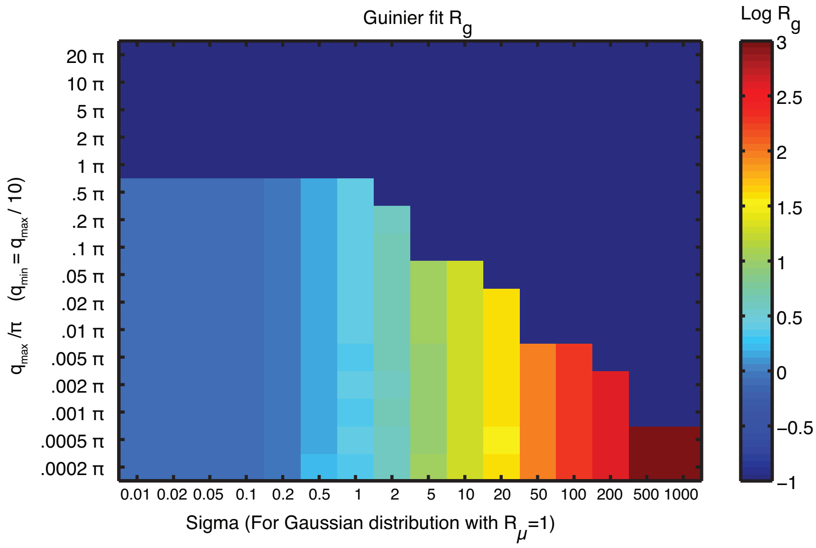
$$I(q) = I_e \bar{N}_p n^2 \exp(-\frac{R_g^2 q^2}{3}) \tag{1}$$

where $I(q)$ is the intensity scattered to wavevector $q = \frac{4\pi \sin\Theta}{\lambda}$, with 2Θ as the scattering angle and λ as the wavelength. I_e is the scattering factor for a single electron, n the number of electrons in a particle, $\bar{N}_p$ the number of particles in the scattering volume and R_g the radius of gyration [1]. This radius of gyration can be computed for a number of particle shapes. The limitations of the method are that it should be applied to dilute, monodisperse and isotropic solutions of particles [2]. Additionally the Guinier method has an upper q limit of validity of around $q \leq 1/R_g$ [3], with the magnitude of the error approaching 20-30 % at $q = 2/R_g$. A detailed study of the deviations of the Guinier method is given in [3], where they also show that the common conception that the aspect ratio of particles needs to be close to unity for the Guinier method to be applicable, may be fallacious.

Despite these limitations, the method has been used widely in the analysis of saxs data in its original form [4], as part of the Beaucage Unified Fit model [5], or as a summation of Guinier terms [6]. It is noted that the Guinier method, when applied to the scattering of polydisperse systems, is strongly biased to the larger particles due to the weighting of the scattered intensity with the radius of the particle to the sixth power [4]. It therefore seems improbable that the Guinier method can be applied to polydisperse systems, a claim well worth verifying.

A test of the Guinier method on simulated data can reveal its applicability on polydisperse systems. For this test, scattering patterns are simulated of systems of polydisperse spheres [7]. The chosen polydispersity shape is Gaussian (cropped to radii of $R \geq 0$), with the mean radius set to 1, and the variance is varied in the range of $0.01 \leq \sigma \leq 1 \times 10^4$. A Guinier fit is attempted over a decade in q-ranges starting from $\frac{2\pi}{0.01} \leq q_{min} \leq \frac{2\pi}{1\times10^3}$ $(q_{max} = 10 q_{min})$. The ranges are divided on a rational (engineering) scale (e.g. $1, 2, 5, 10, 20, 50, \ldots$). After masking out failed fits, the found radii of gyrations are plotted in Figure 1.

From the figure, several conclusions can be drawn. Firstly, the Guinier fit has an upper limit, which reduces when polydispersity comes into play. Secondly, the found radius of



Darlun 1. Radius of gyration found from fits to simulated scattering patterns of polydisperse spheres..

gyration is dependent on the polydispersity. It can be shown that the radius of gyration in polydisperse systems is the volume-square weighted radius of gyration, i.e.:

$$R_{g,\text{weighted}} = \frac{\int V(R_g)^2 P(R_g) R_g \mathrm{d}R_g}{\int V(R_g)^2 P(R_g) \mathrm{d}R_g} \tag{2}$$

Where $R_{g,\text{weighted}}$ is the weighted radius of gyration and R_g the particle radius of gyration. V is the volume of the particle, and $P(r)$ is the probability distribution function. It is easier in some cases to calculate the weighted radius first, according to:

$$r_{\text{weighted}} = \frac{\int V(r)^2 P(r) r \mathrm{d}r}{\int V(r)^2 P(r) \mathrm{d}r} \tag{3}$$

and then calculate the weighted radius of gyration from the weighted radius.

The upper limit of q_{max} to which the Guinier method can be applied appears to be close to $q_{max} = 1.3 R_{g,\text{weighted}}$. Thus, the limit of applicability quickly shifts into the USAXS regions for polydisperse systems, where interparticle scattering effects, collimation imperfections and air- and solvent scattering effects become significant contributors. For polydisperse systems, then, the Guinier method may no longer be the easiest to apply.

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[7] This was done using the "perfectpattern_spheres" program available on the lookingatnothing.com website.