The Guinier method in polydisperse systems - Revised

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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:

$$I(q) \propto \exp(-\frac{R_g^2 q^2}{3}) \tag{1}$$

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. R_g is here the radius of gyration [1].

The original limitations of the method were that it be applied to dilute, monodisperse and isotropic solutions of particles [2]. The Guinier method can describe the data up to a q limit of approximately $q \leq 1/R_g$, with the magnitude of the error approaching 20-30 % at $q = 2/R_g$ [3]. A detailed study of the deviations of the Guinier method is given by [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 used in the TBT by [6–8]. Unfortunately for the latter (TBT-like) applications, it is not possible to simply superimpose multiple Guinier relationships in order to extract a distribution shape for a unimodal distribution.

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 is interesting to see whether the Guinier method can be applied in polydisperse systems. [9] and [10] indicate that it can (with references in page 471 of Otto Glatter's book dating back to 1969), and that the radius of gyration would then be the square root of the volume-squared-weighted mean radius [9]:

$$R_{g,\mu} = \left(\frac{3\langle R^8\rangle}{5\langle R^6\rangle}\right)^{0.5} \tag{2}$$

It is also worth testing how it might relate to the volume-weighed $R_{g,v}$, and the intensity-weighted mean radius of gyration $R_{g,i}$:

$$R_{g,v} = \sqrt{\frac{3}{5}}\frac{\langle R^4\rangle}{\langle R^3\rangle} \tag{3}$$

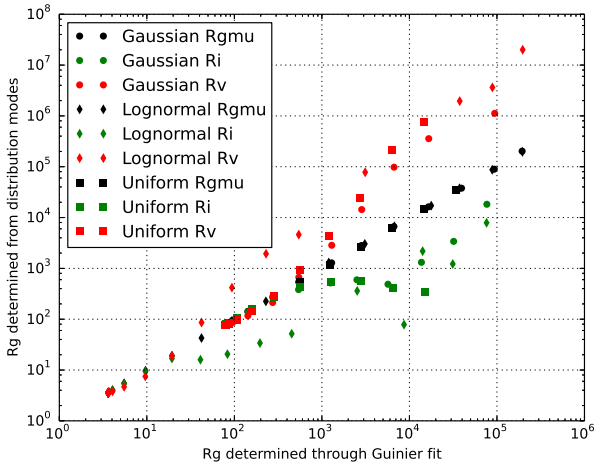

FIG. 1. Radius of gyration found from fits to simulated scattering patterns of polydisperse samples (with a mean of 100, and a range of distribution widths) compared to Rg as calculated using equations 2, 3 and 4.

$$R_{g,i} = \sqrt{\frac{3}{5}}\frac{\langle R^7\rangle}{\langle R^6\rangle} \tag{4}$$

We can easily test this on simulated data of polydisperse systems. For this test, scattering patterns are simulated of using three different shapes of polydispersity distributions, i.e. Gaussian, log-normal and uniform. For each distribution, a range of 20 distribution widths are tested, logarithmically spaced over a span of $1 \times 10^-2 \leq \sigma \leq 1 \times 10^5$ [11]. For each of these distributions, the mean is set to 100. The q-range for fitting is defined by the upper limit $q_{max} = 1/R_{g,\mu}$ (and $1/R_{g,v}$ and $1/R_{g,i}$ for volume- and number-weighted means respectively), and $q_{min} = 0.01 q_{max}$. The scattering patterns are simulated so that the maximum intensity has 1e6 virtual "photons", and the uncertainties are defined by Poisson statistics or 1% of the intensity, whichever is largest (similar to the method used in [12]. The Guinier fit is attempted over the entire q-range as defined above.

From the results shown in figure 1, we can tell a couple of things. Firstly, the Guinier fit applied to patterns from polydisperse systems will assume the radius of gyration as defined in equation 2, in accordance with the statements in literature. Secondly, it is not equal to the volume- or intensity-weighted radius of gyration, which over- and underestimate the expected value from the fit.

Since the q-range appropriate for the Guinier approxi-

mation is defined by the weighted radius, we see that the valid q-range will quickly shift into the USAXS regions for polydisperse systems, a region typically unreachable by normal instruments. It is a good idea, therefore, to step away from using the Guinier method for polydisperse systems, and to use more globally applicable methods instead (i.e. methods that can be applied over the full q-range instead). These give a much milder weighting as explored in section 3 of [12].

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