Debye's expansion of the form factor

For illustrative purposes Debye's expansion of the form factor is presented first. Equation 3 is

$$P(\theta)=\frac{1}{N_{\mathrm{v}}^{2}}\sum_{i}^{N_{\mathrm{v}}}\sum_{j}^{N_{\mathrm{v}}}\frac{\sin(qr_{\mathrm{ij}})}{qr_{\mathrm{ij}}} \tag{3}$$

The Taylor series expansion of the function sin(x)/x is

$$\frac{\sin(x)}{x}=1-\frac{x^{2}}{3!}+\frac{x^{4}}{5!}-\frac{x^{6}}{7!}+\ldots \tag{S.1}$$

Substituting x in eq. S.1 by qr_{ij} and evaluating in eq. 3 gives eq. 6

$$P(\theta)=1-\frac{1}{3}\left[\frac{1}{2N_{\mathrm{v}}^{2}}\sum_{i}^{N_{\mathrm{v}}}\sum_{j}^{N_{\mathrm{v}}}r_{ij}^{2}\right]q^{2}+\frac{1}{60}\left[\frac{1}{2N_{\mathrm{v}}^{2}}\sum_{i}^{N_{\mathrm{v}}}\sum_{j}^{N_{\mathrm{v}}}r_{ij}^{4}\right]q^{4}-\frac{1}{2520}\left[\frac{1}{2N_{\mathrm{v}}^{2}}\sum_{i}^{N_{\mathrm{v}}}\sum_{j}^{N_{\mathrm{v}}}r_{ij}^{6}\right]q^{6}+(Oq^{8}) \tag{6}$$

Derivation of Equation 9

The moment of r_{ij} are defined as

$$\Delta r_{n}=\frac{1}{2N_{\mathrm{v}}^{2}}\sum_{i}^{N_{\mathrm{v}}}\sum_{j}^{N_{\mathrm{v}}}r_{ij}^{n} \tag{S.2}$$

Equation S.2 can be expressed in terms of volume elements rather than scattering elements

$$\Delta r_{n}=\frac{1}{2N_{\mathrm{v}}^{2}}\sum_{i}^{N_{\mathrm{v}}}\sum_{j}^{N_{\mathrm{v}}}r_{ij}^{n}=\frac{1}{2N_{\mathrm{v}}^{2}}\sum_{h}^{N_{\beta}}\sum_{k}^{N_{\beta}}N_{h}N_{k}r_{hk}^{n} \tag{S.3}$$

where r_{hk} is the distance from the center of the volume element h to the center of volume element k, N_{β} is the total number of volume elements h or k in a nanoparticle and N_{h} and N_{k} are the number of scattering elements that are found in each h or k.

If all volume elements h and k have an equal volume ΔV_{h} and ΔV_{k}, and since $N_{\mathrm{v}}^{2} = \Sigma\Sigma 1$, the moment Δr_{n} can be expressed as:

$$\Delta r_n = \frac{\sum_{h}^{N_\beta}\sum_{k}^{N_\beta} N_h N_k r_{hk}^n \Delta V_h \Delta V_k}{2\sum_{h}^{N_\beta}\sum_{k}^{N_\beta} N_h N_k \Delta V_h \Delta V_k} \quad \text{(S.4)}$$

According to Riemann's definition, the integral of function $f(x)$ can be expressed as

$$\int_a^b f(x)\,dx = \lim_{\Delta x_i \to 0} \sum_i^n f(x_i)\Delta x_i \quad \text{(S.5)}$$

Then if the number of scatterers is large enough such that all volume elements are infinitely small, Riemann's definition gives

$$\frac{\sum_{i}^{N_v}\sum_{j}^{N_v} N_i N_j r_{ij}^n \Delta V_j \Delta V_i}{2\sum_{i}^{N_v}\sum_{j}^{N_v} N_i N_j \Delta V_j \Delta V_i} = \frac{\int_V\int_V N_i N_j r_{ij}^n dV_j dV_i}{2\int_V\int_V N_i N_j dV_j dV_i} \quad \text{(S.6)}$$

The number of scatterers N_i in volume element i can be expressed as

$$N_i = \langle N \rangle g(\mathbf{r_i}) \quad \text{(S.7)}$$

where $\langle N \rangle$ is the average number of scattering elements in one volume element, and $g(\mathbf{r_i})$ is the one-body radial distribution function. Substitution of eq. S.7 into eq. S.6 gives eq. 9 from the article

$$\Delta r_n = \frac{1}{2N_v^2}\sum_{i}^{N_v}\sum_{j}^{N_v} r_{ij}^n = \frac{\int_V\int_V g(\mathbf{r_i})g(\mathbf{r_j}) r_{ij}^n dV_j dV_i}{2\int_V\int_V g(\mathbf{r_i})g(\mathbf{r_j}) dV_j dV_i} \quad \text{(8)}$$

Derivation of Equations 10a to 10c

The difference r_{ij} is the magnitude of the vector $\mathbf{r_i}$ - $\mathbf{r_j}$. Then if n is an even number

$$r_{ij}^n = \sqrt{(\mathbf{r_i} - \mathbf{r_j})^{2n}} = (\mathbf{r_i} - \mathbf{r_j})^n \quad \text{(S.8)}$$

and

$$r_{ij}^2 = \left(\mathbf{r_i} - \mathbf{r_j}\right)^2 = r_i^2 + r_j^2 - 2\left(\mathbf{r_i} \cdot \mathbf{r_j}\right) \tag{S.9a}$$

$$r_{ij}^4 = \left(\mathbf{r_i} - \mathbf{r_j}\right)^4 = r_i^4 + r_j^4 + 2r_i^2 r_j^2 - 4\left(r_i^2 + r_j^2\right)\left(\mathbf{r_i} \cdot \mathbf{r_j}\right) + 4\left(\mathbf{r_i} \cdot \mathbf{r_j}\right)^2 \tag{S.9b}$$

$$\begin{aligned} r_{ij}^6 &= \left(\mathbf{r_i} - \mathbf{r_j}\right)^6 \\ &= r_i^6 + r_j^6 + 3\left(r_i^4 r_j^2 + r_i^2 r_j^4\right) - 6\left(r_i^4 + r_j^4 + 2r_i^2 r_j^2\right)\left(\mathbf{r_i} \cdot \mathbf{r_j}\right) + 12\left(r_i^2 + r_j^2\right)\left(\mathbf{r_i} \cdot \mathbf{r_j}\right)^2 - 8\left(\mathbf{r_i} \cdot \mathbf{r_j}\right)^3 \end{aligned} \tag{S.9c}$$

If the coordinates origin is chosen at the center of mass of the nanoparticle, then integration of eqs. S.9a, S.9b and S.9c according to eq. 9 cancel all the terms containing odd powers of ($\mathbf{r_i} \cdot \mathbf{r_j}$). Thus the second, fourth and sixth moments of r_{ij} are

$$\Delta r_2 = \frac{\int_V g(\mathbf{r}) r^2 dV}{\int_V g(\mathbf{r}) dV} \tag{S.10a}$$

$$\begin{aligned} \Delta r_4 = \frac{1}{\int_V \int_V g(\mathbf{r_i}) g(\mathbf{r_j}) dV_i dV_j} \Bigg[&\left(\int_V g(\mathbf{r}) dV\right)\left(\int_V g(\mathbf{r}) r^4 dV\right) + \left(\int_V g(\mathbf{r}) r^2 dV\right)^2 \\ &+ 2\int_V \int_V g(\mathbf{r_i}) g(\mathbf{r_j}) (\mathbf{r_i} \cdot \mathbf{r_j})^2 dV_i dV_j \Bigg] \end{aligned} \tag{S.10b}$$

$$\begin{aligned} \Delta r_6 = \frac{1}{\int_V \int_V g(\mathbf{r_i}) g(\mathbf{r_j}) dV_i dV_j} \Bigg[&\left(\int_V g(\mathbf{r}) dV\right)\left(\int_V g(\mathbf{r}) r^6 dV\right) \\ &+ 3\left(\int_V g(\mathbf{r}) r^4 dV\right)\left(\int_V g(\mathbf{r}) r^2 dV\right) + 12\int_V \int_V g(\mathbf{r_i}) g(\mathbf{r_j}) r_i^2 (\mathbf{r_i} \cdot \mathbf{r_j})^2 dV_i dV_j \Bigg] \end{aligned} \tag{S.10c}$$

If the particle is large enough to consider that it has a uniform mass distribution such that g(**r**)=1, the volume integrals can be taken over the nanoparticle shape and eqs. 10a, 10b and 10c from the article are obtained

$$\Delta r_2 = \frac{1}{V_P} \int_{V_P} r^2 dV \tag{9a}$$

$$\Delta r_4 = \frac{1}{V_P^2} \left[V_P \int_{V_P} r^4 dV + \left(\int_{V_P} r^2 dV \right)^2 + 2 \int_{V_P} \int_{V_P} (\mathbf{r_i} \cdot \mathbf{r_j})^2 dV_j dV_i \right] \tag{9b}$$

$$\Delta r_6 = \frac{1}{V_P^2} \left[V_P \int_{V_P} r^6 dV + 3 \left(\int_{V_P} r^4 dV \right) \cdot \left(\int_{V_P} r^2 dV \right) + 12 \int_{V_P} \int_{V_P} r_i^2 (\mathbf{r_i} \cdot \mathbf{r_j})^2 dV_j dV_i \right] \tag{9c}$$

Derivation of Schulz-Zimm distribution moments

Derivation of the expression for the n-moment of the Schulz-Zimm distribution is done for illustrative purposes. The moments of the distribution should not be confused with Δr_n, which are the moments of the difference of distances within a nanoparticle. The Shulz-Zimm distribution function is

$$w(x) = \frac{h^{k+1}}{\Gamma(k+1)} x^k e^{-hx} \tag{S.11}$$

where h = (k+1)/x_x and k = 1/(PDI_x - 1); x is the x-averaged x and PDI_x is the polydispersity of x defined as x_x/x_n, where x_n is the number average x. The n-moment of the distribution is

$$\left\langle x^n \right\rangle_x = \int_0^\infty w(x) x^n dx = \int_0^\infty \frac{h^{k+1}}{\Gamma(k+1)} x^k e^{-hx} x^n dx \tag{S.12}$$

Equation S.12 can be solved using integration by parts and assigning

$$u = x^{k+n} \qquad du = (k+n) x^{k+n-1}$$

$$dv = \frac{h^{k+1}}{\Gamma(k+1)} e^{-hx} dx \qquad v = \frac{-h^{k+1}}{h\Gamma(k+1)} e^{-hx}$$

thus

$$\begin{aligned}\left\langle x^n\right\rangle_w &= \int_0^\infty \frac{h^{k+1}e^{-hx}}{\Gamma(k+1)}x^{k+n}dx \\ &= -x^{n+k}\frac{h^k e^{-hx}}{\Gamma(k+1)}\bigg|_0^\infty + \frac{(k+n)}{h}\int_0^\infty \frac{h^{k+1}e^{-hx}}{\Gamma(k+1)}x^{k+n-1}dx = \frac{k+n}{h}\int_0^\infty \frac{h^{k+1}e^{-hx}}{\Gamma(k+1)}x^{k+n-1}dx\end{aligned} \tag{S.13}$$

Integrating by parts n times gives

$$\left\langle x^n\right\rangle_w = \int_0^\infty \frac{h^{k+1}e^{-hx}}{\Gamma(k+1)}x^{k+n}dx = \frac{(k+n)(k+n-1)\ldots(k+n-(n-1))}{h^n}\int_0^\infty \frac{h^{k+1}e^{-hx}}{\Gamma(k+1)}x^{k}dx \tag{S.14}$$

The integral in the last term corresponds to ∫w(x)dx = 1, thus the moment of the Schulz-Zimm distribution is

$$\left\langle x^n\right\rangle_w = \int_0^\infty w(x)x^n dx = \int_0^\infty \frac{h^{k+1}e^{-hx}}{\Gamma(k+1)}x^{k+n}dx = \frac{(k+n)!}{h^n k!} = \frac{x_x^n(k+n)!}{(k+1)^n k!} \tag{S.15}$$

Equation 12 of the article arises from eq. S.15

$$\int_0^\infty\int_0^\infty\int_0^\infty w(A)w(B)w(C)A^nB^mC^p dAdBdC = \left[\frac{A_A^n(k_A+n)!}{(k_A+1)^n k_A!}\right]\left[\frac{B_B^m(k_B+n)!}{(k_B+1)^m k_B!}\right]\left[\frac{C_C^p(k_C+n)!}{(k_C+1)^m k_C!}\right] \tag{11}$$

Form factor of rectangular parallelepipeds and triaxial ellipsoids

The form factor of a rectangular parallelepiped with Axis A, B and C is[1]

$$P(q,a,c) = \int_0^1 \phi_Q\left(\mu\sqrt{1-\sigma^2},a\right)\left[\frac{\sin(\mu c\sigma/2)}{\mu c\sigma/2}\right]^2 d\sigma \tag{S.16}$$

where

$$\phi_Q(\mu,a) = \int_0^1 \left\{\frac{\sin\left[\frac{\mu}{2}\cdot\cos\left(\frac{\pi}{2}\cdot u\right)\right]}{\frac{\mu}{2}\cdot\cos\left(\frac{\pi}{2}\cdot u\right)}\cdot\frac{\sin\left[\frac{\mu a}{2}\cdot\sin\left(\frac{\pi}{2}\cdot u\right)\right]}{\frac{\mu a}{2}\cdot\sin\left(\frac{\pi}{2}\cdot u\right)}\right\}^2 du \tag{S.17}$$

$\mu = qB$, $a = A/B$, $c = C/B$ and $q = (4\pi n_S/\lambda_0)\sin(\theta/2)$

The form factor of a triaxial ellipsoid with semiaxis a, b and c is[2]

$$P(q,a,b,c) = \int_0^1 \int_0^1 \phi^2 \left\{ q \left[a^2 \cos^2(\pi x/2) + b^2 \sin^2(\pi x/2)\left(1-y^2\right) + c^2 y^2 \right]^{1/2} \right\} dxdy \tag{S.18}$$

where

$$\phi^2(t) = 9\left(\frac{\sin t - t\cos t}{t^3} \right)^2 \tag{S.19}$$

and a < b < c

References

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2. Feigin, L. A.; Svergun, D. I. In *Structure Analysis by Small-Angle X-Ray and Neutron Scattering;* Taylor, G. W., Ed.; Plenum Press: New York, 1987; pp 90-94.