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Robert Botet, Sylvie Kwok and Bernard Cabane

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– Supplementary Information –

Robert Botet,[a*] Sylvie Kwok[b] and Bernard Cabane[b]

[a]*Laboratoire de Physique des Solides Bât.510,*

CNRS UMR8502 / Université Paris-Saclay, Centre d'Orsay, F-91405 Orsay France,

and [b]*CBI, ESPCI, CNRS, PSL University, 75005 Paris France.*

E-mail: robert.botet@u-psud.fr

1. Reformulation of the Vrij solution for the structure factor of an assembly of hard spheres

We consider a two-phase system made of non-deformable spheres (e.g. phase O) dispersed in a liquid (phase W). The overall volume fraction of phase O is φ. Each sphere is supposed homogeneous and spherical, and its radius is noted a. The population of polydisperse spherical particles has a normalized radius-distribution $n(a)$ (normalization condition: $\int_0^\infty n(a)da = 1$).

Let q be the magnitude of the scattering vector in a small-angle scattering experiment. The normalized intraparticle interference factor of a homogeneous sphere of radius a, is noted: $\Phi(qa)$, with the function $\Phi(x) = 3(\sin x - x\cos x)/x^3$. The scattering amplitude contributed by the spherical particle of radius a is then: $\alpha_3 a^3 \Phi(qa)$, in which α_3 is a coefficient dependent on the refractive indices of the two phases. We also introduce the function $\Psi(x) = \sin x/x$.

The static structure factor, $S(q)$, of such a system is generally written as:

$$S(q) = \frac{\varphi_0}{\varphi} \frac{I_\varphi(q)}{I_{\varphi_0}(q)} \ , \tag{1}$$

in which $I_\varphi(q)$ is the normalized intensity scattered by the system at the volume fraction φ, and $I_{\varphi_0}(q)$ the scattering intensity of the same system when diluted to an extremely small volume fraction $\varphi_0 \simeq 0$. In (1), the coefficient φ/φ_0 is the dilution factor.

In the following steps, we use notations close to (Vrij, 1979), except for the definition of the averaged values of quantities related to the particle radii. Below, the averaged value of a quantity $F(a)$ depending on the radius a, is the standard one, namely:

$$\Big\langle F(a) \Big\rangle \equiv \int_0^\infty F(a)\, n(a) da \ . \tag{2}$$

The analytical results obtained by Vrij for a polydisperse population of spheres are:

$$R_\varphi(q) = \frac{-D_f(q)}{\Delta(q)} \ , \tag{3}$$

$$-\frac{(1-\varphi)^4}{\varphi} D_f(q) = A_0 \Big(\Big\langle a^6 \Phi^2 \Big\rangle |T_1 + T_2|^2 + \Big\langle a^4 \Psi^2 \Big\rangle |T_3|^2 + $$

$$+ \Big\langle a^5 \Phi \Psi \Big\rangle ((T_1 + T_2) T_3^\star + (T_1^\star + T_2^\star) T_3) \Big) \ , \tag{4}$$

$$(1-\varphi)^4 \Delta(q) = |T_1|^2 \ , \tag{5}$$

in which A_0 is a normalization coefficient independent of q and of φ but dependent on the electromagnetic properties of the emulsion and of the radius distribution. To be precise, $A_0 = 16\alpha_3^2/(4\pi\Big\langle a^3 \Big\rangle/3)$. The auxiliary functions T_1, T_2, T_3 are given by the following expressions (Vrij, 1979):

$$F_{11} = 1-\varphi\left(1-\frac{\left\langle a^3\Phi e^{iqa}\right\rangle}{\left\langle a^3\right\rangle}\right)\ , \tag{6}$$

$$F_{22} = 1-\varphi\left(1-3\frac{\left\langle a^3\Psi e^{iqa}\right\rangle}{\left\langle a^3\right\rangle}\right)\ , \tag{7}$$

$$F_{12} = \varphi\frac{\left\langle a^4\Phi e^{iqa}\right\rangle}{\left\langle a^3\right\rangle}\ , \tag{8}$$

$$F_{21} = (1-\varphi)iq-3\varphi\frac{\left\langle a^2\right\rangle-\left\langle a^2\Psi e^{iqa}\right\rangle}{\left\langle a^3\right\rangle}\ , \tag{9}$$

$$T_1 = F_{11}F_{22}-F_{12}F_{21}\ , \tag{10}$$

$$T_2 = \varphi\left(F_{21}\frac{\left\langle a^4\Phi e^{iqa}\right\rangle}{\left\langle a^3\right\rangle}-F_{22}\frac{\left\langle a^3\Phi e^{iqa}\right\rangle}{\left\langle a^3\right\rangle}\right)\ , \tag{11}$$

$$T_3 = 3\varphi\left(F_{12}\frac{\left\langle a^3\Phi e^{iqa}\right\rangle}{\left\langle a^3\right\rangle}-F_{11}\frac{\left\langle a^4\Phi e^{iqa}\right\rangle}{\left\langle a^3\right\rangle}\right)\ . \tag{12}$$

These expressions lead to the structure factor function under the form:

$$S(q) = \frac{(1-\varphi)^2}{|T_1|^2}\left(|F_{22}|^2+9\frac{\left\langle a^4\Psi^2\right\rangle}{\left\langle a^6\Phi^2\right\rangle}|F_{12}|^2-\right. \tag{13}$$

$$\left.-3\frac{\left\langle a^5\Phi\Psi\right\rangle}{\left\langle a^6\Phi^2\right\rangle}(F_{22}F_{12}^\star+F_{22}^\star F_{12})\right)\ , \tag{14}$$

where we used the relations derived from (6), (8), (10), (11):

$$T_1+T_2 = (1-\varphi)F_{22}\ , \tag{15}$$

$$T_3 = -3(1-\varphi)F_{12}\ . \tag{16}$$

To continue the calculation, it is now convenient to introduce the following functions:

$$f_{11} = 1+\psi\frac{s_0+s_1}{\nu_3}\ , \tag{17}$$

$$f_{22} = 1+\psi\frac{s_2}{\nu_3}\ , \tag{18}$$

$$f_{12} = \psi\frac{s_1}{\nu_3}\ , \tag{19}$$

where:

$$\psi = \frac{3\varphi}{1-\varphi} \ , \tag{20}$$

$$\nu_3 = \Big\langle (qa)^3 \Big\rangle \ , \tag{21}$$

$$\Xi(x) = \sin x - x\cos x \ , \tag{22}$$

$$s_0 = \Big\langle \Xi(qa)\, e^{iqa} \Big\rangle \ , \tag{23}$$

$$s_1 = -\, i \Big\langle qa\, \Xi(qa)\, e^{iqa} \Big\rangle \ , \tag{24}$$

$$s_2 = \Big\langle (qa)^2 \, \sin(qa)\, e^{iqa} \Big\rangle \ . \tag{25}$$

That way, one obtains the identity:

$$|T_1|^2 = (1-\varphi)^4 \left| f_{11} f_{22} + f_{12}^2 \right|^2 \ , \tag{26}$$

hence the expression of the structure factor:

$$S(q) = \frac{\Big\langle \Xi^2 \Big\rangle |f_{22}|^2 + \mathrm{Im}\{s_2\}|f_{12}|^2 - i\mathrm{Re}\{s_1\}(f_{22}^\star f_{12} - f_{22} f_{12}^\star)}{\Big\langle \Xi^2 \Big\rangle \left| f_{11} f_{22} + f_{12}^2 \right|^2} \ . \tag{27}$$

At last, one uses the following identities:

$$\psi \Big\langle \Xi^2 \Big\rangle = \mathrm{Im}\{f_{11}\} \ , \tag{28}$$

$$\psi \mathrm{Im}\{s_2\} = \mathrm{Im}\{f_{22}\} \ , \tag{29}$$

$$\psi \mathrm{Re}\{s_1\} = \mathrm{Re}\{f_{12}\} \ , \tag{30}$$

to put the expression of the structure factor under the compact form:

$$S(q) = \frac{\mathrm{Im}\{f_{22}^\star (f_{11} f_{22} + f_{12}^2)\}}{\mathrm{Im}\{f_{11}\} |f_{11} f_{22} + f_{12}^2|^2} \ , \tag{31}$$

in which the three auxiliary complex-valued functions f_{11}, f_{22}, f_{12} are defined by:

$$f_{11} = 1 + \psi \, \frac{\mu_1}{\nu_3} \ , \tag{32}$$

$$f_{22} = 1 + \psi \, \frac{\mu_2}{\nu_3} \ , \tag{33}$$

$$f_{12} = \psi \, \frac{\mu_3}{\nu_3} \ , \tag{34}$$

with the parameter ψ given in (20). Generally, the parameters $\mu_1, \mu_2, \mu_3, \nu_3$ do not depend on the volume fraction φ of the scattering matter. They are given explicitly by the following formulae:

$$\mu_1 = \Big\langle (1 - iqa)\,(\sin(qa) - qa\cos(qa))\, e^{iqa} \Big\rangle \ , \tag{35}$$

$$\mu_2 = \Big\langle (qa)^2 \, \sin(qa)\, e^{iqa} \Big\rangle \ , \tag{36}$$

$$\mu_3 = -\, i \Big\langle qa\,(\sin(qa) - qa\cos(qa))\, e^{iqa} \Big\rangle \ , \tag{37}$$

$$\nu_3 = \Big\langle (qa)^3 \Big\rangle \ . \tag{38}$$

An equivalent form of the set of formulae (31)-(38), using only real-valued functions, is given in the Section 2. It results simply from rewriting (31) with $f_{11} = \mathrm{Re}\{f_{11}\} + i\,\mathrm{Im}\{f_{11}\}$ and similar expressions for f_{22} and f_{12}.

The auxiliary parameter μ_1 has another role in the context of scattering intensity. Indeed, using the same quantities, the diluted scattering intensity of the polydisperse system, is:

$$I_0 \propto \frac{\Big\langle \, (\sin(qa) - qa\cos(qa))^2 \, \Big\rangle}{q^6} \ , \tag{39}$$

in which the proportionality constant is independent of q for a constant wavelength. Using (28), I_0 can be written under the form:

$$I_0 \propto \frac{\mathrm{Re}\{\mu_1\}}{q^6} \ . \tag{40}$$

comparison with published results

- In (van Beurten & Vrij, 1981), the authors showed structure factor functions calculated from an assembly of hard spheres with a Schulz distribution of the particle diameters and various values of standard deviation. The original solution proposed by Vrij (Vrij, 1979) is used. Their FIG. 4, for example, corresponds to data for the volume fraction $\varphi = 0.1$ with diameter standard deviations

$= 0$ (monodisperse case), $0.1, 0.3$ and 1.0. The Schulz distribution with mode $\left\langle 2a \right\rangle = 1$ is used, that is:

$$n_{\text{Schulz}}(a) \propto \left(ae^{-2a}\right)^{b-1} \quad , \tag{41}$$

with the following relation between the positive exponent b and the standard deviation, σ_a, of the radius distribution:

$$\sigma_a = \frac{\sqrt{b}}{2(b-1)} \ . \tag{42}$$

The monodisperse case corresponds to $b \to \infty$.

The results obtained from the results given in the Section 4.1 for the Schulz distribution with $\varphi = 0.1$ and the three values of the standard deviations used in (van Beurten & Vrij, 1981) are shown in our FIG. 1. The results are similar to previously published data.

- In (Scheffold & Mason, 2009), the authors compared their experimental data to the analytical solution presented in (Ginoza & Yasutomi, 1999) for the structure factor of a polydisperse system with a Schulz diameter distribution. Using the same set of parameters, one finds our FIG. 2 which can be compared to their Figure 1.

2. formulae for some radius-distributions using the complex-valued auxiliary quantities (35)-(37)

2.1. the Schulz distribution

The case of Schulz distribution:

$$n_{\text{Schulz}}(a) \propto \ a^{s-1}e^{-s\,a/\langle a\rangle} \ , \tag{43}$$

is discussed in details in the Section 4.1. We give here the complete solution for $S_{\text{Schulz}}(q)$ in terms of the complex-valued auxiliary functions μ_1, μ_2, μ_3, in order to obtain a solution in a more compact form.

Let us introduce the auxiliary function μ_0:

$$\mu_0 = \frac{e^{i(s+2)\tan^{-1}2x}}{(1+4x^2)^{s/2+1}} \ , \tag{44}$$

and the scaled variable $x = q\left\langle a\right\rangle/s$.

The auxiliary parameters μ_1, μ_2, μ_3 are such that:

$$\begin{aligned}\mu_1 = \ & \frac{i}{2}\Big[1 + s(s+1)x^2 - \\ & -\mu_0\left(1 - 2(s+2)ix - (s+1)(s+4)x^2\right)\Big] \ ,\end{aligned} \tag{45}$$

$$\mu_2 = \frac{ix^2}{2} s(s+1)\left(1-\mu_0\right) \ , \tag{46}$$

$$\mu_3 = \frac{sx}{2}\Big(1 + i(s+1)x - \mu_0(1 - i(s+3)x)\Big) \ , \tag{47}$$

and

$$\nu_3 = s(s+1)(s+2)x^3 \ . \tag{48}$$

One can notice that when the value of the parameter s is an integer number, the expression of μ_0 is quite simple:

$$\mu_0 = \frac{1}{(1-2ix)^{s+2}} \ . \tag{49}$$

Consequently, $S_{\mathrm{Schulz}}(q)$ can in this case be expressed as the ratio of two polynomials in x. For example:

$$s = 1 \Rightarrow \mu_0 = \frac{1 - 12x^2 + 2ix(3-4x^2)}{(1+4x^2)^3} \ , \tag{50}$$

$$s = 2 \Rightarrow \mu_0 = \frac{1 - 24x^2 + 14x^4 + 8ix(1-4x^2)}{(1+4x^2)^4} \ , \tag{51}$$

etc.

and the static structure factor, $S_{\mathrm{Schulz}}(q)$, is obtained readily from expression (31).

2.2. the power-law distribution

The power-law radius distribution is defined as:

$$n_{\text{power-law}}(a) \propto \frac{1}{a^{d_f+1}} \quad \text{for} \quad a_{\min} < a < a_{\max} \ . \tag{52}$$

The exponent d_f is here restricted to the values $2 < d_f < 3$. The auxiliary positive parameter: $\rho \equiv a_{\min}/a_{\max}$ is used henceforth, introduced by the relation:

$$1 - \varphi \simeq \kappa \, \rho^{3-d_f} \ , \tag{53}$$

as conjectured in (Varrato & Foffi, 2011), and κ is a number with value of order 1. At last, we define the parameter w as:

$$w = \frac{1-\varphi}{\kappa - (1-\varphi)} \ . \tag{54}$$

The values of the first moments of the radius are calculated:

$$\left\langle a \right\rangle = \frac{d_f}{d_f - 1} \, a_{\min} \left(\frac{1 - \rho^{d_f-1}}{1 - \rho^{d_f}} \right) \ , \tag{55}$$

$$\left\langle a^2 \right\rangle = \frac{d_f}{d_f - 2} \, a_{\min}^2 \left(\frac{1 - \rho^{d_f-2}}{1 - \rho^{d_f}} \right) \ , \tag{56}$$

$$\left\langle a^3 \right\rangle = \frac{d_f}{3 - d_f} \, a_{\min}^3 \frac{1}{\rho^{3-d_f}} \left(\frac{1 - \rho^{3-d_f}}{1 - \rho^{d_f}} \right) \ . \tag{57}$$

Note the term ρ^{d_f-3} in expression (57), which may be quite large in the case of wide power-law distributions (that is when $\rho \ll 1$).

Defining the reduced variable:

$$x \equiv q a_{\min} \ , \tag{58}$$

the expressions for μ_1, μ_2, μ_3 can be expressed after introducing the auxiliary function μ_0 written in terms of the incomplete Gamma function, $\Gamma(.,.)$, namely:

$$\mu_0(x) = \frac{\sin x}{x} e^{ix} + (-2ix)^{d_f-3} \Gamma(3 - d_f, -2ix) \ , \tag{59}$$

$$\frac{\mu_k}{\nu_3} = w\,\frac{3-d_f}{d_f-2}\left[\varphi_k(x) - \rho^{d_f-3}\varphi_k(x/\rho)\right] \qquad ; \qquad k=1,2,3 \quad , \tag{60}$$

$$\begin{aligned}\varphi_1(x) = {} & i\,\frac{d_f-2}{2\,d_f}\left(\frac{1+2x^2-e^{2ix}(1-2ix)}{x^3}\right) + \\ & +\frac{4-d_f}{d_f}\mu_0(x)\ ,\end{aligned} \tag{61}$$

$$\varphi_2(x) = \mu_0(x)\ , \tag{62}$$

$$\varphi_3(x) = i\,\frac{d_f-2}{2(d_f-1)}\left(\frac{2x-i(1-e^{2ix})}{x^2}\right) + \frac{3-d_f}{d_f-1}\mu_0(x)\ . \tag{63}$$

It is interesting to note that when $\rho \ll 1$, all the quantities $\rho^{d_f-3}\varphi_k(x/\rho)$ appearing in the above formulae are negligible, since $\varphi(x) \sim 1/x$ in $x \to 0$, for all the three indices $k=1,2,3$, and $d_f > 2$. In addition, all the quantities in parenthesis in the moments (55)-(57) are $\simeq 1$. Taking into account these approximations, and taking the real values of all quantities, we can then recover the formulae (74)-(83).

Acknowledgements

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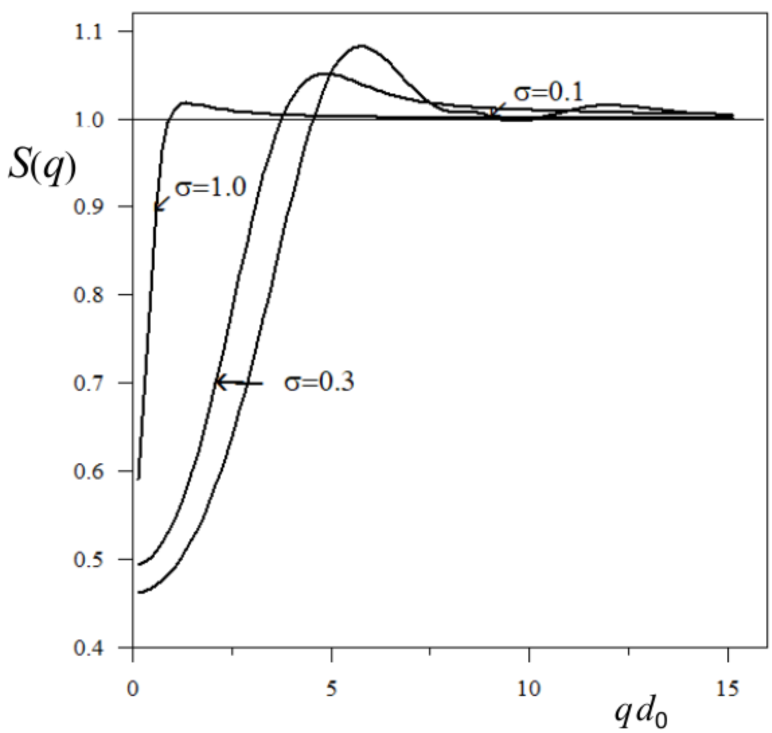

Fig. 1. Structure factor $S(q)$ at volume fraction $\varphi = 0.1$ for several standard deviations σ of hard-sphere diameters. The notation $d_0 = 2\left\langle a \right\rangle$ is used. These data are to be compared with FIG. 4 of reference (van Beurten & Vrij, 1981).

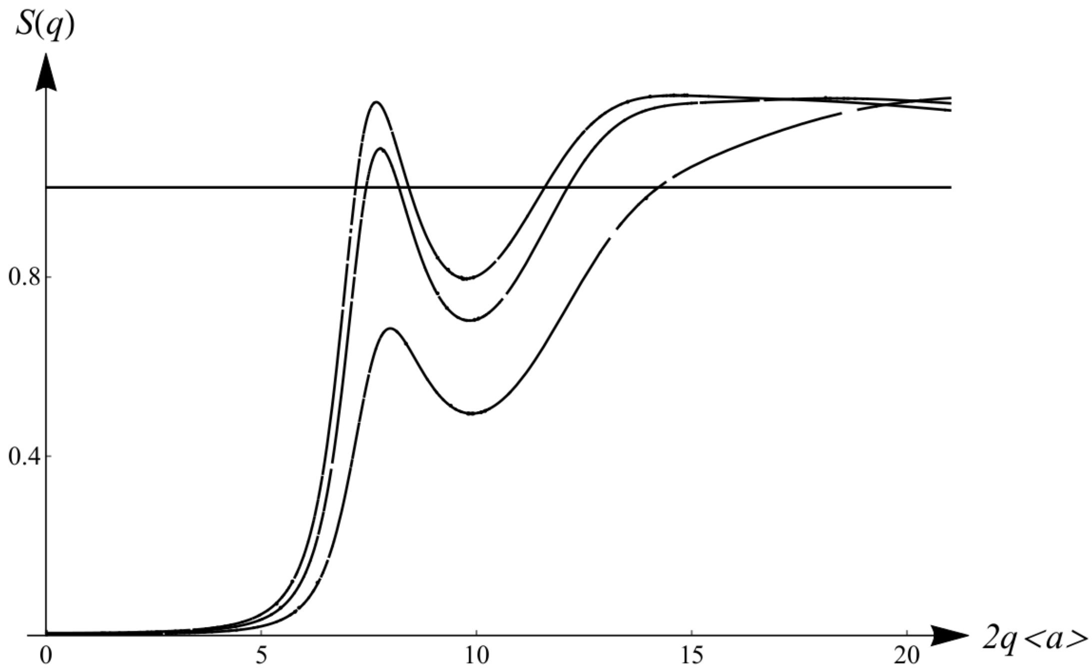

Fig. 2. Scaled static structure factor function $S(q)$ at volume fractions and parameters: ($\varphi = 0.7$; $s = 23.34$), ($\varphi = 0.72$; $s = 24.27$), ($\varphi = 0.77$; $s = 22.68$), respectively (from top to bottom). These data have to be compared with Figures 1.a), b), c) of reference (Scheffold & Mason, 2009).