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Short Communication

Scattering by a network of prolate, cross-section-polydispersed cylinders applicable to fibrillar thermoreversible gels(*)

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Abstract. — The intensity scattered by a network of cross-section-polydispersed cylinders in which the mesh size is far larger than the largest cross-sectional radius is calculated by considering a weight distribution function of the type \( w(r) \sim r^{-\lambda} \) with two cut-off radii, \( r_{\text{min}} \) and \( r_{\text{max}} \). Two scattering ranges are identified (transitional range and Porod-range). The case \( \lambda = 1 \) is particularly detailed as it corresponds to existing experimental cases. It is shown that the different radii \( r_{\text{min}}, r_{\text{max}}, r_n \) (number-averaged), \( r_w \) (weight-averaged) can be determined independently of the intensity absolute calibration.

1. Introduction.

The numerous investigations carried out on the morphology of thermoreversible gels have shown arrays of fiber-like structures [1-10]. While the mesh size of these networks is about 1 \( \mu \)m, the maximum fiber cross-section is but of a few tens of nanometres.

Schematically speaking, these structures may be regarded as random assemblies of prolate cylinders. While in some cases the fiber cross-sections are defined in a very narrow range of values, such as \( \kappa \)-carrageenans for instance [10], in many cases there is a broad distribution of cross-sections, a striking and illustrative example being poly-L-benzyl glutamate gels [3].

The effect of polydispersity has already been worked out for chemically-formed clusters characterized by a fractal dimension \( D \). Whereas monodispersed clusters should scatter as \( q^{-D} \), it has been shown that polydispersity alters the exponent \( D \), yielding an apparent fractal dimension whose value depends upon the chosen type of distribution [11, 12].

The aim of this short paper is to adopt the same type of approach with cross-section-polydispersed cylinders so as to work out the intensity in the range where it is affected by the cross-section scattering effects. This range is usually accessible by means of small-angle neutron or small-angle X-ray scattering techniques.

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2. Theoretical.

A weight distribution function \( w(r) \) for the cylinder cross-sections with two cut-off radii, namely \( r_{\text{max}} \) and \( r_{\text{min}} \) is considered here. If \( l_n \) is the network mesh size, a simple analytical expression for the scattered intensity can be derived under the following conditions:

\[
ql_n \gg 1(q = 4\pi/\lambda \sin \theta/2)
\]
\[
l_n \gg r_{\text{max}}
\]

The calculation can then be achieved by considering dilute, infinitely-long cylinders. These conditions hold for many thermoreversible gels in the vicinity of the critical gelation concentration.

2.1 TRANSITIONAL q-RANGE. — In this q-range the transfer momentum range is such that the product \( qr \) can take any value (hence the name transitional q-range): for low \( r \) values \( qr < 1 \) while for large values \( qr > 1 \). No simple expansion of the scattering function can be carried out and one has to integrate over the entire distribution to work out the scattered intensity.

For infinite cylinders of cross-sectional radius \( r \) the absolute intensity reads [13]:

\[
I_{\text{Ai}}(q)/C_i = 4\pi \mu_{\text{Li}} J_1^2(q_{\text{ri}})/(q^3 r^2) \quad (1)
\]

where \( C_i \) is the concentration and \( \mu_{\text{Li}} \) is the mass per unit length (in g/mole×nm) of cylinders of cross-sectional radius \( r_i \), and \( J_1 \) the Bessel function of first kind and order 1. If one assumes that all cylinders are of the same nature, then \( \mu_{\text{Li}} \) is proportional to \( r_{i}^3 (\mu_{\text{Li}} = \alpha r_{i}^3 = \pi \rho r_{i}^3 \), where \( \rho \) is the molecular density in g/mole×nm\(^3\)). For a distribution of cylinder cross-section the intensity is written:

\[
I_{\text{A}}(q)/C = 4\alpha \pi q^{-3} \times \sum w_i J_1^2(qr_i) \quad (2)
\]

where \( C \) is the global polymer concentration and \( w_i \) the weight fraction of species possessing a cross-sectional radius \( r_i \). Equation (2) can be written in the case of a continuous distribution:

\[
\frac{I_{\text{A}}(q)}{C} = \frac{4\pi \alpha}{W q^2} \times \int_{r_{\text{min}}}^{r_{\text{max}}} w(r) J_1^2(qr) dr \quad (3)
\]

where \( W \) is:

\[
W = \int_{r_{\text{min}}}^{r_{\text{max}}} w(r) dr \quad (4)
\]

The weight distribution \( w(r) \) of interest here is:

\[
w(r) \sim r^{-\lambda} \quad (5)
\]

This implies that the total length of cylinders with cross-sectional radius \( r \) in the scattering volume, \( L_T(r) \), varies as \( r^{-(\lambda+2)} \) since \( w(r) \sim L_T(r)r^2 \).

The integral in relation (3) can be evaluated by parts by subtracting integrals from 0 to \( r_{\text{min}} \) and from \( r_{\text{min}} \) to \( \infty \) from the integral from 0 to \( \infty \) for which an analytical solution exists provided \( 0 < \lambda < 3 \) [14]:

\[
\int_{0}^{\infty} J_1^2(qr)r^{-\lambda} dr = \frac{\Gamma(\lambda)\Gamma\left(\frac{3-\lambda}{2}\right)}{2^\lambda \Gamma\left(\frac{\lambda+1}{2}\right) \Gamma\left(\frac{\lambda+3}{2}\right)} \times q^{\lambda-1} = A(\lambda) \times q^{\lambda-1} \quad (6)
\]
where \( \Gamma \) is the gamma function.

For integrating from 0 to \( r_{\text{min}} \), the Bessel function can be expanded for \( qr \ll 1 \) provided that \( qr_{\text{min}} \ll 1 \). Only the first term needs then to be taken into account. Integration from \( r_{\text{max}} \) to \( \infty \) can be achieved by expanding the Bessel function for \( qr \gg 1 \). The terms of higher order of the development of the Bessel function can be dropped on the condition \( qr_{\text{max}} \gg 1 \).

The intensity finally reads in a \( q^4 I_A(q) \) vs. \( q \) representation:

\[
\frac{q^4 I_A(q)}{C} = \frac{4\pi \alpha}{W} \left[ A(\lambda)q^\lambda - \frac{1}{\lambda \pi r_{\text{max}}^\lambda} - q^3 r_{\text{max}}^3 - \lambda \right]
\]

As the transfer momentum range is such that \( qr_{\text{min}} \ll 1 \), the last term in equation (7) can now be dropped provided it is negligible with respect to \( A(\lambda)q^\lambda \).

\( \lambda = 1 \) is of particular interest as a simple linear variation is obtained, a case which pertains to PVC gels [15] and poly-hexyl-isocyanate gels [16]:

\[
\frac{q^4 I_A(q)}{C} = \left[ 2\pi \alpha q - \frac{4\alpha}{r_{\text{max}}} \right] \times \log^{-1} \left( \frac{r_{\text{max}}}{r_{\text{min}}} \right) \quad \text{for } \lambda = 1
\]

Interestingly, the scattering vector \( q_0 \) for which \( q^4 I_A(q) = 0 \) is related to \( r_{\text{max}} \) through a simple relation independent of the calibration procedure of the scattered intensity:

\[
r_{\text{max}} = \frac{2}{\pi q_0} \simeq \frac{0.637}{q_0} \quad \text{for } \lambda = 1
\]

As will be seen below, it is convenient to define the following quantity from the slope of relation (8):

\[
\sigma = \frac{q^4 I_A(q = Q_0) - q^4 I_A(q = 0)}{2\pi^2 C Q_0} = \rho \times \log^{-1} \left( \frac{r_{\text{max}}}{r_{\text{min}}} \right) \quad \text{for } \lambda = 1
\]

2.2 Porod q-range. — If the minimum cross-sectional radius \( r_{\text{min}} \) were close to nought, then relation (7) would account for the scattering in the whole \( q \)-range. On account of this minimum value, there exists a \( q \)-range where \( qr_{\text{min}} \gg 1 \). In this domain, referred to as the Porod domain, the intensity oscillates around an asymptote which, by expanding the Bessel function for \( qr \gg 1 \), is written:

\[
\frac{4\pi \rho}{q^4} \left[ 1 + \frac{3}{8q^2 r^2} + \ldots \right]
\]

Integrating relation (11) over the cross-sectional radius distribution gives:

\[
\frac{q^4 I_A(q)}{C} = \frac{4\pi \rho}{W} \int_{r_{\text{min}}}^{r_{\text{max}}} \left[ \frac{1}{r} + \frac{3}{8q^2 r^3} \right] w(r)dr
\]

For \( \lambda = 1 \) relation (12) is by neglecting \( (1/r_{\text{max}})^3 \) with respect to \( (1/r_{\text{min}})^3 \):

\[
\frac{q^4 I_A(q)}{C} = 4\pi \rho \times \left[ \frac{1}{r_n} + \left( 8q^2 r_{\text{min}}^3 \log \frac{r_{\text{max}}}{r_{\text{min}}} \right)^{-1} \right] \quad \text{for } \lambda = 1
\]

where \( r_n \) is the number-averaged cross-section radius.
As a rule, unless very small radii are dealt with, the second term is negligible. It is convenient to define the following quantity from the plateau regime:

\[ \sigma_0 = \frac{q^4 I_A(q)}{4\pi C} = \frac{\rho}{r_n} \text{ for } \lambda = 1 \] (14)

Again, for \( \lambda = 1 \), \( r_n \) is written:

\[ \frac{1}{r_n} = \left[ \frac{1}{r_{\text{min}}} - \frac{1}{r_{\text{max}}} \right] \times \log^{-1} \left( \frac{r_{\text{max}}}{r_{\text{min}}} \right) \text{ for } \lambda = 1 \] (15)

It follows from relations (10), (14) and (15) for \( \lambda = 1 \):

\[ \frac{r_{\text{max}}}{r_{\text{min}}} = \frac{\sigma_0 r_{\text{max}}}{\sigma} + 1 \text{ for } \lambda = 1 \] (16)

As relation (9) allows one to determine \( r_{\text{max}} \) without ambiguity, \( r_{\text{min}}, r_n \) and \( \rho \) can be also straightforwardly obtained. It should be further noted that the determination of \( r_{\text{max}}, r_{\text{min}} \) through relations (9), (15) and (16) is independent of the absolute calibration.

Another parameter worth calculating is the weight-averaged cross-section radius, \( r_w \).

\[ r_w = \frac{1}{W} \int_{r_{\text{min}}}^{r_{\text{max}}} r w(r) dr = \left( r_{\text{max}} - r_{\text{min}} \right) \times \log^{-1} \left( r_{\text{max}} / r_{\text{min}} \right) \text{ for } \lambda = 1 \] (17)

2.3 **Effect of Cylinder Interscattering.** — So far the theoretical expression for the intensity has been worked out on the basis of diluted cylinders. The condition \( q l_n \gg 1 \) implies that one has to consider all the scattering objects located within a sphere of radius smaller than \( l_n \). As its center is not fixed, the sphere is liable to contain “junctions” or “crossings” between fibers (see Fig. 1). This will give an additional scattering (cross-terms) which needs to be evaluated. Only the terms between direct neighboring fibers have to be considered.

![Fig. 1. Schematic two-dimensional representation of a fibrillar network. The differing line thicknesses schematize the different cross-sectional radii. The circles whose radius is \( q^{-1} \) illustrate the range of distances explored. The dotted circle shows the case where there is a “junction” in the range of investigated distances. The condition \( q l_n \gg 1 \) implies that only one junction at a time can be in this circle (which is a sphere in the three-dimensional space).](image-url)
In the transitional range one is dealing with infinitely-long cylinders. Consider two cylinders whose long-axes cross at point O. Be A and B two points on cylinders 1 and 2 respectively, the scattering amplitude can be written:

\[ A(q) = A_0 \exp(-i q \cdot OA) + A_0 \exp(-i q \cdot OB) = A_1(q) + A_2(q) \]  

(18)

Defining the angles \( \theta_1 \) and \( \theta_2 \) between the scattering vector and the cylinder long axis and using the approach by Fournet [17] eventually gives for the cross-term:

\[ A_1(q)A_2(q) \approx \int_{0}^{\pi/2} \int_{0}^{\pi/2} \frac{\sin(qL_1 \cos \theta_1)2J_1(qr \sin \theta_1)}{qL_1 \cos \theta_1 qr \sin \theta_1} \cdot \frac{\sin(qL_2 \cos \theta_2)2J_1(qr \sin \theta_2)}{qL_2 \cos \theta_2 qr \sin \theta_2} \sin \theta_1 \sin \theta_2 d\theta_1 d\theta_2 \]  

(19)

If the angle between the axes of the two cylinders were allowed to vary at random, then the integrals in relation (19) could be calculated separately. Yet, as the system is frozen, the angle between cylinder 1 and cylinder 2 is fixed. Thanks to this condition, it can be shown that the cross-term vanishes for infinitely-long cylinders because the function \( \sin(qL \cos \theta)/(qL \cos \theta) \) becomes rapidly zero except for [18, 19]:

\[ q \cos \theta = 0 \]  

(20)

In other words, the scattering vector has to be perpendicular to the cylinder axis otherwise the intensity drops very rapidly. As the probability for two neighbouring fibers to possess simultaneously the right orientation to fulfill relation (20) is very low, the cross-terms can be ignored in this range.

The situation differs in the Porod-range in which the infinitely-long cylinder characteristic plays no longer a role as the system scatters as any two-density medium. Cross-terms have to be taken into account as can be illustrated by considering the derivation made by Kirste and Porod [20]. For a medium with two main curvatures \( C_1 \) and \( C_2 \) these authors have derived the

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**Fig. 2.** — Example of experimental scattering pattern in a \( q^4 I(q) \) vs. \( q \) representation for PVC/diethyl oxalate gels (\( C_{PVC} = 5 \times 10^{-2} \ g/cm^3 \) [from Ref. [15]]. This case can be interpreted with \( \lambda = 1 \). From the intersect of the straight line obtained in the transitional \( q \)-range with the \( q \)-axis, one derives \( r_{max} = 10.6 \ nm \), which value agrees with electron microscopy findings [4]. Use of relations (15) and (16) gives \( r_{min} = 2.2 \ nm \) and \( r_n = 4.4 \ nm \).
following equation:

\[ I(q) \approx \frac{1}{q^4} \left[ 1 + \frac{\langle C_1 C_2 \rangle}{q^2} + \frac{3/8}{q^2} <(C_1 - C_2)^2> \right] \]  

(21)

in which the brackets denote the averaging over all the sample.

For a cylinder, one curvature is identical to zero so that one retrieves relations (11). Yet, when cylinders cross one another both curvatures differ from zero. This will result in enhancing the terms of degree higher than 4 so that, in the \( q^4 I(q) \) vs. \( q \) representation, the terminal \( q^{-4} \) behaviour will be reached from above instead of being reached from below.

Figure 2 shows an illustrative, experimental case (PVC gels [15]) for which \( \lambda = 1 \) pertains.

3. Concluding remarks.

Calculations presented in this paper allow determination of the fiber cross-sectional dimensions provided that the weight distribution function of cross-sectional radii obeys a simple power law. Interestingly, absolute calibration is not required for determining the different cross-sectional radii. This theoretical analysis applies quite successfully to the case of PVC gels [15] and poly hexyl isocyanate gels [16] with \( \lambda = 1 \). The advantage of the scattering method lies in its non-destructive characteristic as it allows investigation of the sample in its unperturbed, three-dimensional state unlike electron microscopy which, in routine investigations, gives a distorted, two-dimensional picture of the gels. Despite electron microscopy shortcomings, this technique is nevertheless necessary to ensure that the gels possess a fiber-like structure which is a prerequisite for applying the above equations.

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