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The Exponential Distribution in Small Angle X-Ray Scattering. Theory and Practice*

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Summary. From all the theoretical small-angle X-ray scattering (SAXS) curves of compact (non-particulate) systems elaborated systematically by Porod [2], we give a theoretical analysis of only one scattering curve, the corresponding correlation function of which is an exponential distribution. To obtain a correct as well as an easier determination of the zero-intensity I_0 and the correlation length l_c than with the procedure usual up to now (analysis of the plot $I(s)^{-1/n}$ vs. s^2 with $n = 2$ or 3/2) the classical SAXS-parameters of particle scattering will be involved in the evaluation. In this way the results get also a more useful conception for a practical application.

Keywords. Small-angle X-ray scattering (SAXS); Exponential distribution.

Die exponentielle Verteilung in der Röntgenkleinwinkelstreuung. Theorie und Praxis

Von den systematisch besprochenen Röntgenkleinwinkelstreukurven der dichtgepackten Systeme von Porod [2] wird nur eine Streukurve, deren Korrelationsfunktion eine exponentielle Verteilung aufweist, theoretisch analysiert und mit den klassischen Auswertungsmethoden der Partikelstreuung in Verbindung gesetzt. Dadurch werden die die Streukurve bestimmenden Parameter l_c (Kohärenzlänge) und die Nullintensität I_0 besser erfaßt als mit der in der Literatur bisher veröffentlichten Methode (Auftragung $I(s)^{-1/n}$ gegen s^2, mit $n = 2$ oder 3/2). Damit erhalten außerdem die Meßergebnisse eine anschaulichere Auslegung.

Introduction

Description of the Exponential Distribution

In the zero-order Poisson distribution the random variable r is said to have the standard exponential distribution if its probability density function at r, in conventionally abbreviated form, is

$$\gamma(r) = \begin{cases} 0 & \text{for } r < 0 \\ a\exp(-ar) & \text{for } r \geqslant 0 \end{cases}$$

in which a is an adjustable, positive and real number, called the *parameter of the distribution.* This distribution is referred to either as the negative exponential or

* Dedicated to Prof. Dr. Dr. h.c. mult. Otto Kratky on the occasion of his 90th birthday

simply as the exponential. In the following we use the second version. The expectation value of the distribution is $E(r) = 1/a$ and the variance $V(r) = 1/a^2$.

The exponential distribution is generally well-known to describe the radio-active disintegration or among others the appearing of defects in matter. In his theoretical publication [2] Porod systematically studies the small-angle X-ray scattering (SAXS) curves of various compact (or non-particulate) systems, and shows that in some cases the self-convolution of the electron density distribution in the system, the so-called characteristic function or correlation function corresponds to an exponential distribution as well, e.g. gel-structure with increasing concentration. Earlier Debye and Bueche found the same by the light scattering study of Lucite and two glass samples [1]. Utilizing the exponential distribution as a correlation function in SAXS (or in small-angle scattering in general), the random variable r signifies the distance, measured from an arbitrary point in the matter. The parameter of the distribution, a, is now the reciprocal value of a mean distance. This distance is defined [3] as the half of the integral breadth l_c of the correlation function ($l_c/2 \equiv 1/a$). l_c is the so-called coherence- or correlation length defined by Porod [4]. It is known that the *reduced** chord length or intersection length l_r, defined also by Porod [5], can be obtained by differentiating the correlation function at $r \to 0$. In our case (normalized exponential function) the differentiation always gives [3]

$$(\gamma(r)/\gamma(0))' = (\gamma_0(r))' = -a \equiv -1/l_r.$$

Therefore, we obtain for the exponential distribution and *only for this distribution*, an important relation between its correlation length l_c and its reduced chord length l_r

$$2l_r = l_c$$

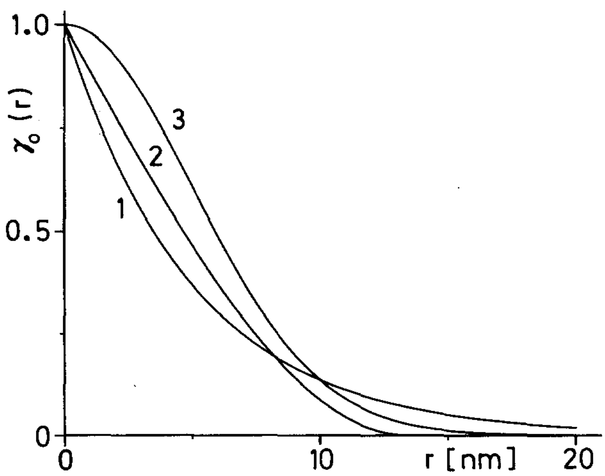

Fig. 1. *1* the correlation function with exponential distribution $\gamma_0(r) = \exp(2r/l_c)$, $l_c = 10$ nm; *2* the correlation function of a sphere, $\gamma_0(r) = 1 - 3x/2 + x^3/2$, $x = r/D$, with the diameter $D = 13.3$ nm, corresponding to $l_c = 10$ nm, and *3* Gaussian function with $2\sigma = l_c = 10$ nm

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* The reduced chord length l_r is closely related to the (average) lengths l_1 and l_2 of the chords crossing phase 1 and phase 2, respectively in the arbitrarily chosen direction ($l_r^{-1} = l_1^{-1} + l_2^{-1}$) [5]

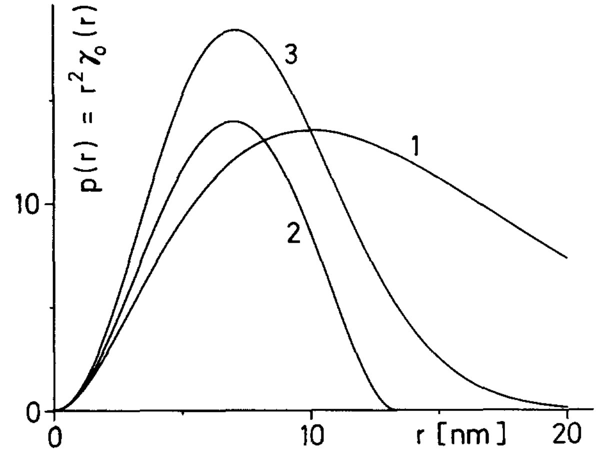

Fig. 2. The distance distribution functions ($p(r) = r^2\gamma_0(r)$) of the curves of Fig. 1. *1* exponential function, *2* sphere, and *3* Gaussian function

and the distribution takes the simple form

$$\gamma_0(r) = \exp(-r/l_r) = \exp(-2r/l_c). \tag{1}$$

Figure 1 visualizes the exponential distribution, Eq. (1), with $l_c = 10\,\text{nm}$ ($a = 1/l_r = 2/l_c = 0.2\,\text{nm}^{-1}$) and compares it with the correlation function of a sphere ($\gamma_0(r) = 1 - 3x/2 + x^3/2$, $x = r/D$) with the diameter $D = 13.3\,\text{nm}$ (corresponding to $l_c = 10\,\text{nm}$; $D = (4/3)l_c$) and with a normalized Gaussian probability distribution having the same variance ($\gamma_0(r) = \exp(-a^2r^2/2)$). Figure 2 shows the distance distribution functions ($p(r) = r^2\cdot\gamma_0(r)$) of the same models (distance distribution functions are frequently utilized in the SAXS analysis).

For practical reasons we note here the moments (the n^{th} moment of the distribution $f(x)$ is $M_n = \int x^n f(x)\,\mathrm{d}x$) and some other useful statements of this distribution (Table 1).

The Fourier Transformation of the Exponential Distribution

The spherically symmetric Fourier transformation of the exponential distribution $\gamma_0(r)$ gives the distribution of scattered intensity (scattering curve) of the studied

Table 1. The moments and other parameters of the exponential function Eq. (1)

Moments

$M_{\tau_0} = l_c/2 = l_r$,	$M_{\tau_1} = l_c^2/4 = l_r^2$
$M_{\tau_2} = l_c^3/4 = 2l_r^3$,	$M_{\tau_3} = 3l_c^4/8 = 6l_r^4$
$M_{\tau_4} = 3l_c^5/4 = 24l_r^5$,	$M_{\tau_n} = \int r^n \exp(-2r/l_c)\,\mathrm{d}r = n!(l_c/2)^{n+1}$

Deduced values

Center of gravity $= l_c/2 = l_r$, integral width $= l_c/2 = l_r$,
breadth at half maximum $= \ln 2\, l_c/2 = 0.3466 l_c = 0.6931 l_r$,
$\sigma = l_c/2 = l_r$, variance $= l_c^2/4 = l_r^2$,
$M_{\tau_2}/M_{\tau_0} = l_c^2/2 = 2l_r^2$, $M_{\tau_2}/M_{\tau_1} = l_c = 2l_r$

system. Using the coordinate $x = s$ for the scattering curve, we have

$$\begin{aligned} I(s) &= 2s^{-1}\int r\cdot\gamma_0(r)\sin 2\pi rs\,\mathrm{d}r \\ &= 2s^{-1}\int r\exp(-2r/l_c)\sin 2\pi rs\,\mathrm{d}r = I_0/(1+(\pi s l_c)^2)^2, \end{aligned} \tag{2}$$

$s = 2\sin\theta/\lambda$, λ = wave length of the monochromatic X-ray. $I(s)$ is the scattered intensity at the coordinate s, without the influence of the collimating slit system (pin-hole collimation or desmeared scattering curve), and the value of $I(s)$ at $s = 0$, I_0, is the so-called zero angle intensity. The Hankel transformation (of zero order) of the exponential distribution delivers the scattered intensity $\tilde{I}(s)$, which we obtain with a slit system whose slit length is very large compared to the slit width perpendicular to the slit length ($\tilde{I}(s)$ is the s.c. "smeared" scattering curve of $I(s)$):

$$\tilde{I}(s) = 2\pi\int r\exp(-2r/l_c)\cdot J_0(2\pi rs)\,\mathrm{d}r = \tilde{I}_0/(1+(\pi s l_c)^2)^{3/2}, \tag{3}$$

J_0 is the Bessel function of zero order, $\tilde{I}_0$ the intensity at zero angle of the smeared curve.

Tables 2 and 3 present the necessary parameters for the characterization of the scattering curves (2) and (3).

The well known [6] general mathematical relations between the moments M_n and $\tilde{M}_n$ of the scattered and smeared intensities ($I(s)$ and $\tilde{I}(s)$) and between those and the correlation function $\gamma_0(r)$ can be confirmed in the case of the exponential function also. Three important relations for the following practical considerations should be kept in mind:

(a) $\tilde{I}_0 = 2M_0$ therefore $\tilde{I}_0/I_0 = \pi/2b$, (b) $I_0 = 2M_2M_{\tau 2}/\pi$, (c) $\tilde{M}_1 = 2M_2$, (4)

where b is defined in the note to Tables 2 and 3.

Table 2. Parameters of the scattered intensity curve $I(s)$ corresponding to the exponential correlation function

Moments
$M_0 = I_0\pi/4b$, $M_1 = I_0/2b^2$, $M_2 = I_0\pi/4b^3$
Deduced values
Center of gravity $= 2/\pi b$, integral width $= \pi/4b$,
breadth at half maximum $= (\sqrt{2}-1)^{1/2}/b$, $\sigma = \sqrt{1-4/\pi^2}/b = 0.7712/b$,
variance $= b^{-2}(1-4/\pi^2) = 0.5947/b^2$, $M_2/M_0 = 1/b^2$, $M_1/M_2 = 2b/\pi$

Table 3. Parameters of the smeared intensity curve $\tilde{I}(a)$

$\tilde{M}_0 = \tilde{I}_0/b$, $\tilde{M}_1 = \tilde{I}_0/b^2$, integral width $= 1/b$
Breadth at half maximum $= \sqrt{2^{2/3}-1}/b = 0.7664/b$

Note to Tables 2 and 3: $b = \pi l_c/\lambda a$, or $= \pi l_c$, or $l_c/2$ when the coordinate x is given in m ($= 2a\theta$), or in s ($= 2\sin\theta/\lambda$), or in h ($= 4\pi\sin\theta/\lambda$), respectively. θ = Bragg angle, a = distance from the sample to the plane of registration, λ = wave length. I_0 is the scattered intensity at the angle $\theta = 0$, and $\tilde{I}_0$ likewise that of the smeared one (so-called zero angle intensities)

The Relation Between $I(x)$ and $\tilde{I}(x)$

In the case of the exponential distribution of the correlation function, the pure (not smeared) scattering curve with the coordinate x, $I(x)$ and its smeared one, $\tilde{I}(x)$ (Fig. 3) are related in a simple way. We put Eq. (3) in Eq. (2) (using the general case $s = x$) and we have the desmeared curve $I(x)$ from the smeared one

$$I(x) = (I_0/\tilde{I}_0^{4/3})\cdot\tilde{I}(x)^{4/3},$$

and with (4a) and M_0 from Table 2

$$I(x) = (2b/\pi)\tilde{I}_0^{-1/3}\cdot\tilde{I}(x)^{4/3}.$$

Or, in the same manner, we can obtain from the pure theoretical distribution the smeared one:

$$\tilde{I}(x) = (\tilde{I}_0/I_0^{3/4})\cdot I(x)^{3/4} \quad \text{and} \quad \tilde{I}(x) = (\pi/2b)I_0^{1/4}\cdot I(x)^{3/4}.$$

As before (see note to Tables 2 and 3) $b = \pi l_c/\lambda_a$, or πl_c, or $l_c/2$ when the variable x is given in m or in s or in h.

The Classical Evaluation of $I(0)$, $\tilde{I}(0)$ and l_c

The classical evaluation of the scattering curve $I(x)$ (or $\tilde{I}(x)$, Eqs. (2) or (3)) is the plot $I(x)^{-1/2}$ vs. x^2 (or $\tilde{I}(x)^{-2/3}$ vs. x^2). The straight line with the slope t serves as an extrapolating function to obtain the zero intensity I_0 (or $\tilde{I}_0$) at the angle zero. From this zero intensity and from the slope the parameter l_c can be calculated. We have from (2) (or (3)) with $n = 2$ (for $I(s)$) or $n = 3/2$ or (for $\tilde{I}(s)$)

$$I(x)^{-1/n} = I_0^{-1/n} + I_0^{-1/n}b^2x^2 \tag{5}$$

which gives

$$I_0^{-1/n} \text{ at } x = 0,$$

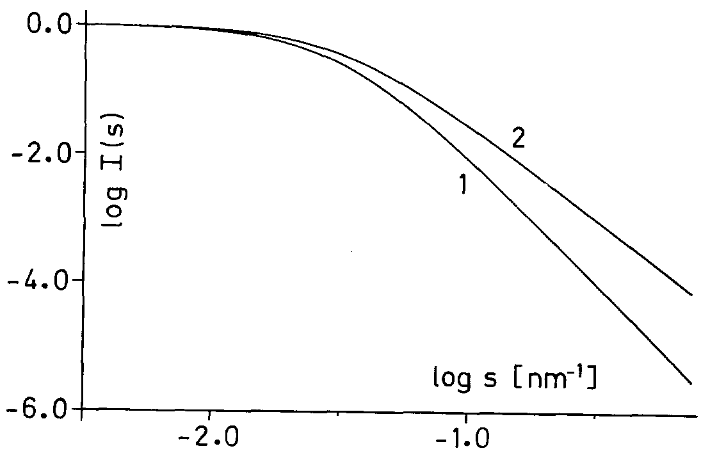

Fig. 3. The scattering curve of a sample with an exponential distribution of its correlation function in the plot $\log(I(s))$ vs. $\log(s)$ obtained *1* with a pin-hole collimation system (unsmeared curve), *2* with a Kratky-camera (smeared intensity curve)

and with the slope

$$t = I_0^{-1/n} b^2 \tag{5a}$$

we obtain

$$b = I_0^{1/2n} \sqrt{t}.$$

But this extrapolation to the zero angle intensity is sometimes a delicate problem. We will discuss it in more detail at the end of this article.

Practical Evaluation of the Scattering Curve in the Case of the Exponential Distribution of Its Correlation Function

The *Guinier plots* and the *Guinier domains*; the relation between the *radius of gyration* R_x and the *length of coherence* l_c.

The approximation of the innermost part of any SAXS curve $I(s)$ with a Gaussian distribution $I_{Gx}(s)$ was introduced by Guinier [7] originally for identical particles for which all orientations are equally probable. The Gaussian approximation of certain *sections* of any scattering curve in a *modified* form ($I_q(s) = sI(s)$ or $I_d(s) = s^2 I(s)$) was elaborated by Porod [8]. In all three cases of the approximation the parameter of the Gaussian functions is R_x. These are the radius of the gyration of the whole phase (R_v), or of its cross section (R_q), or of its thickness (R_d), respectively. The normalization factors I_{0x} are the intensity of the Gaussian curves at $s = 0$ angle. They are proportional to the volume of the phase, in the case of I_{0v}, or to the cross section surface F, in the case of I_{0q}, finally to the thickness D of the phase in the case of I_{0d}, therefore, the general approximating function is:

$$I_{Gx}(s) = I_{0x} \exp((-2\pi s)^2 \cdot R_x^2) \tag{6}$$

with $R_x^2 = R_v^2/3$ for $x = v$ and $R_x^2 = R_q^2/2$ or $R_x^2 = R_d^2$ for $x = q$ or d, respectively. R_x and I_{0x} are always to be determined from the corresponding intensity curve $I_x(s)$ in the plot $\ln(I_x(s))$ vs. s^2 (Guinier plot). The straight line in these plots designs the domain of the validity of the Gaussian approximation ("Guinier domain") in which $I_x(s) = I_{Gx}(s)$. To visualize this region, it is also instructive to draw a plot $\delta I(s) = I_{Gx}(s) - I_x(s)$ vs. s (cf. Fig. 4).

The scattering curve corresponding to the exponential correlation function, Eq. (2), possesses also well defined Guinier regions (Fig. 4). The coordinates of the Guinier points depend on the value of l_c (Table 4). By equality of the relations (2) and (6), at the coordinate of the "Guinier point" s_{Gx}, we find that $s_{Gq} = 1/\pi l_c$ and $s_{Gd} = 5/e\pi l_c$, $e = 2.718\ldots$. Table 4 gives also the practical limits of the Guinier domains in s (nm^{-1}) and in m (cm).

Table 4 and Fig. 4a show that (except in extreme cases such as very small correlation length or very small entrance slit) the Guinier approximation can practically never be applied on the simple intensity curve $I(s)$. The Guinier region for the evaluation of R_v lies in the innermost part of the curve $I(s)$ which is generally not accessible for the measurement (e.g. for an entrance slit 60 mμ and $l_c \approx 10$ nm, the first measured point on the curve is nearly the last one of the Guinier region (Fig. 4a)). On the other hand, we find in Table 4 and Fig. 4c that the intensity curve of the thickness $I_d(s) = s^2 I(s)$ possesses a wide Guinier region around the

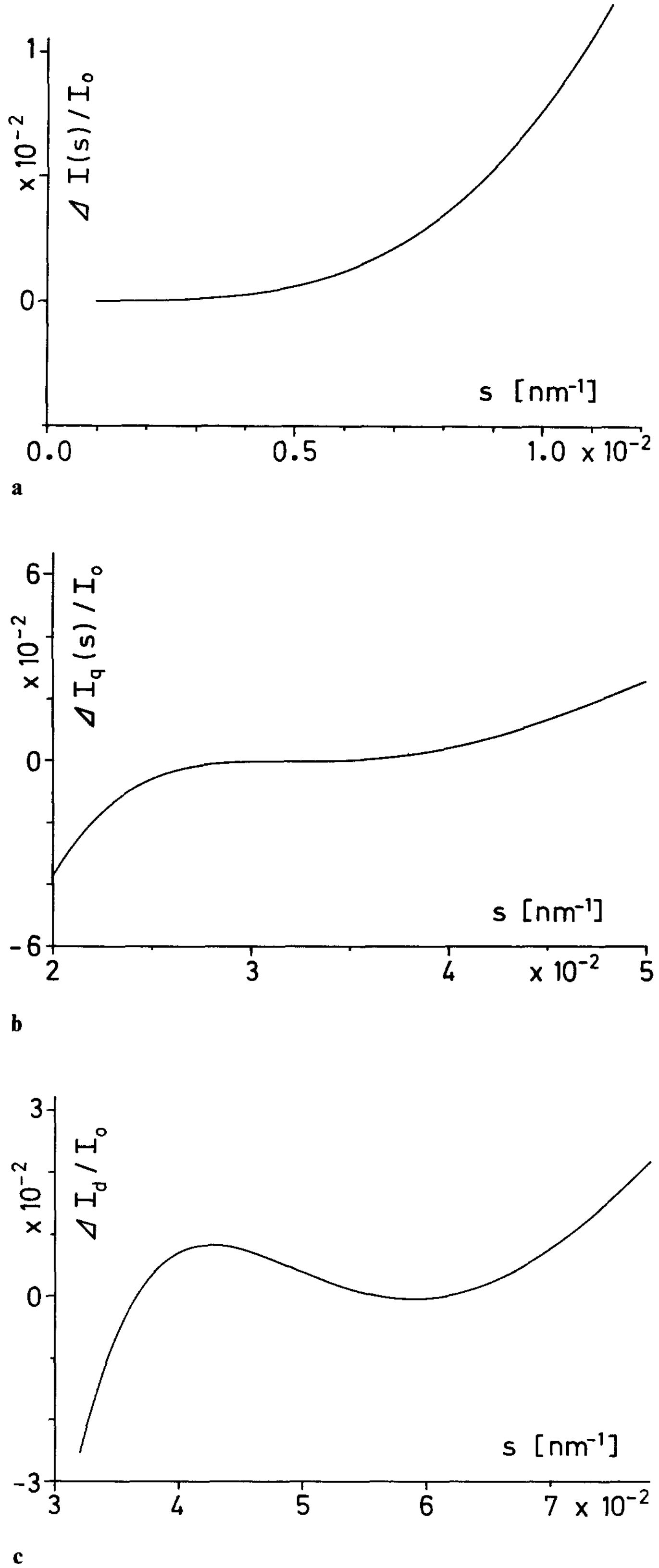

Fig. 4. The three Guinier domains of the scattering curve with an exponential distribution of its correlation function presented as the difference $\delta I_x(s)$ between the scattering curve $I_x(s)$ and the approximating Gaussian curve $I_{Gx}(s)$. $l_c = 10$ nm. **a** $\delta I(s) = I(s) - I_G(s)$; **b** $\delta I(s) = I_q(s) - I_{Gq}(s)$; **c** $\delta I(s) = I_d(s) - I_{Gd}(s)$. The curves are normalized for $I_{G0} = 1$

Table 4. The values in the table are calculated. For the Guinier region $\pm 0.6\%$ deviations from the Gaussian curve were admitted. To have the correct coordinate the values on the table must be divided by l_c in nm. The values in m (cm) are for the sample-detector distance $a = 22$ cm (see the note to Tables 2 and 3)

	l_c·coordinate of Guinier point		l_c·length of Guinier region	
	s_{Gx} [nm^{-1}]	m_{Gx} [cm]	s [nm^{-1}]	m [cm]
On the				
intensity curve $I(s)$	0.0	0.0	0.0–0.11	0–0.38
intensity curve of the cross-section $I_q(s) = sI(s)$	0.32	1.1	0.21–0.38	0.7–1.3
intensity curve of the thickness $I_d(s) = s^2 I(s)$	0.58	1.7	0.35–0.65	1.2–2.2

Guinier point, which is very easy to observe on the Guinier-plot. Also the Guinier region of the cross-section curve $I_q(s) = sI(s)$ is equally good to evaluate for $l_c \leqslant 10$ nm (Fig. 4 b).

To find a relation between R_v and l_c, we develop (2) and (6) in series and we put $I(s) = I_G(s)$. We obtain

$$R_v = (3/2)^{1/2} l_c = 1.225 l_c.$$

The same result is delivered by the well known formula established with the help of the moments of the correlation function. The moments are tabulated in Table 1:

$$R_v^2 = M_{\tau 4}/2M_{\tau 2} = (3/2) l_c^2.$$

In a similar way as above the apparent radius of gyration related to the smeared scattering intensity, $\tilde{R}$, is obtained from (3) and (6)

$$\tilde{R} = (3/2\sqrt{2}) l_c = 1.0607 l_c,$$

therefore

$$R_v = 2\tilde{R}/\sqrt{3}.$$

The evaluation of the radius of the gyrations of $I_q(s)$ and $I_d(s)$ with a given l_c shows that

$$R_q = l_c/2 \quad \text{and} \quad R_d = l_c/5. \tag{7}$$

The Volume V, the Cross-Section Surface F, and the Thickness D

In the case of the particle scattering, which we obtain from a monodisperse infinitely diluted system, the volume V, the cross-section surface F, and the thickness D have a concrete geometrical meaning concerning one well defined particle with a given geometrical form in the system. On the other hand, the scattering curve due to an exponential correlation function will not represent a geometrical behaviour (shape and size) of one of the inhomogeneities (phase 1) in the matrix (phase 2) [5]. The system is a *random scatterer* [10].

This scattering curve is determined only by two parameters: by the correlation length l_c and by the zero intensity I_0 in absolute units. We have seen in (1) that l_c is a parameter of a statistical distribution the so-called zero-order Poisson distribution. Therefore, the length l_c and the corresponding spatial structure are difficult to visualize.

Nevertheless, it is mathematically possible to define – without ambiguity – "volume", "cross-section", "thickness" and other parameters usual in the case of the particle scattering, for this system too: the volume

$$V = (1/4\pi)I_0/M_2 \tag{8a}$$

will be, in our special case, with M_2 in s from the Table 2

$$V = \pi l_c^3. \tag{8b}$$

Similarly we have, from the modified intensity curves, the cross section surface F, from the s.c. cross-section intensity curve $I_q(s) = sI(s)$, and from the intensity curve of the thickness $I_d(s) = s^2 I(s)$ the thickness of the inhomogeneity D:

$$F = (1/2\pi)I_{q0}/M_2 = 2\pi(I_{q0}/I_0)l_c^3 \tag{9}$$

and

$$D = (1/2)I_{d0}/M_2 = 2\pi^2(I_{d0}/I_0)l_c^3 \tag{10}$$

with $I_{q0} = sI(s)$ at $s = 0$ and $I_{d0} s^2 I_{d0}$ at $s = 0$ obtained from a Guinier-type extrapolation of the intensity curves $I_q(s)$ and $I_d(s)$, respectively (see above). It is very easy to find that in this case the relative zero-intensities have simple relations at this intensity curve:

$$I_{q0}/I_0 = \sqrt{e}/4\pi l_c \quad \text{and} \quad I_{d0}/I_0 = 1/2\sqrt{e}\pi^2 l_c^2, \tag{11a, b}$$

therefore

$$I_{q0}/I_{d0} = e\pi l_c/2 \quad \text{with } e = 2.718\ldots. \tag{12}$$

From (9) with (11a) and from (10) with (11b) we find the very simple relations for the cross-section surface and for thickness:

$$F = (\sqrt{e}/2)l_c^2 \tag{13}$$

and

$$D = l_c/\sqrt{e}. \tag{14}$$

Therefore $\sqrt{F}/D = (\sqrt{e}/2)^{1/2} \cdot \sqrt{e} = 1.4969$ and is independent from I_{0x} and l_c.

The great importance of the relations (11a) and (11b), and (13) and (14) is to obtain the zero-intensities I_{0x} and the coherence length l_c of the system from other parameters of the curve than those derived from the classical evaluation (plot $I(s)^{-1/n}$ vs. s^2) (also see below). It must be noted also that multiplication of the so defined F and D values does not give the volume $V = \pi l_c^3$ of the inhomogeneity. We have from (13) and (14) $FD = l_c^3/2 = V/2\pi$ and $F/D = el_c/2$.

The Porod Tail and the Relative Inner Surfaces O_s and S_s in the System

Porod [5a] enunciated the important principle that the tail end of the scattering curve should conform to the asymptotic course of s^{-4}: $I(s) \approx K_p s^{-4}$. K_p is the constant of Porod and is correlated with the relative inner surface of one inhomogeneity (O_s) and with the relative inner surface of the system (S_s):

$$O_s = S_s/w_1 w_2 = 2\pi^2 K_P/M_2.$$

We find from Eq. (2) for $s \to \infty$ and with M_2 from Table 2 that

$$s^4 I(s) = K_P = I_0/b^4 = I_0/(\pi l_c)^4, \tag{15}$$

therefore

$$O_s = 8/l_c \quad \text{and} \quad S_s = 8 w_1 w_2/l_c; \tag{16}$$

w_1 and w_2 are the volume fractions of the phases ($w_1 + w_2 = 1$), which are to be determined from SAXS measurement (9), or with other physical methods (e.g. absorption measurements).

It should be remarked that the slope t from Eq. (5a) and the Porod-constant K_P from (15) are connected in a simple way:

$$t = b^2/I_0^{1/n} \quad \text{and} \quad K_P = I_0/b^4 \text{ give } t = K_P^{-1/n} \tag{17a}$$

with $n = 2$. Similarly to (17a) from the slope t of the smeared intensity curve we have

$$\tilde{K}_P = \tilde{I}_0/b^3 \quad \text{and} \quad \tilde{t} = \tilde{K}_P^{-1/n} \tag{17b}$$

with $n = 3/2$. Eq. (17a) (or (17b)) is an important relation for the evaluation, because K_P is generally easier to determine than t.

Molecular Weight

The normalized scattered intensity at zero angle is correlated with the molecular weight M. The correlation depends only on the normalized zero intensity of the curve ($M \approx I_0/P$, P = normalization factor), and not on the form of the scattered intensity curve. Therefore, it is independent of the distribution of the electron density and thus from the correlation length l_c. For a very general treatment of this problem the reader is referred to a basic paper by Kratky [9].

Determination of the Zero Intensity I_0

The zero angle intensity, rich in information (molecular weight, volume of the inhomogeneity, correlation length) can never be measured directly in SAXS. To obtain it, we utilize in general an extrapolation of the innermost part of the scattering curve to the scattering angle zero. In the case of the classical (pure) particle scattering the Gaussian distribution (Guinier-plot) is unequivocally the theoretically correct extrapolation function. As we have seen, this remains valid in our distribution too. The application is, however, limited to lower l_c values and/or very small entrance slits, because the Guinier-domain is too short and, therefore, difficult to measure. The plot of the Eq. (5) ($(I(s)^{-1/2}$ vs. s^2 (or $\tilde{I}(s)^{-2/3}$ vs. s^2)) is the usual and theoretically correct extrapolation to angle zero in this case. Nevertheless the determination of the zero angle intensity with Eq. (5) will always remain a delicate problem because the diagram presents the root of the reciprocal values of the intensities and the relative error of I_0 becomes great by reading $I_0^{-1/2}$ on the diagram. A least square approximation of the straight line is very sensitive to the limits of the measured curve and to the method of the elimination of the background.

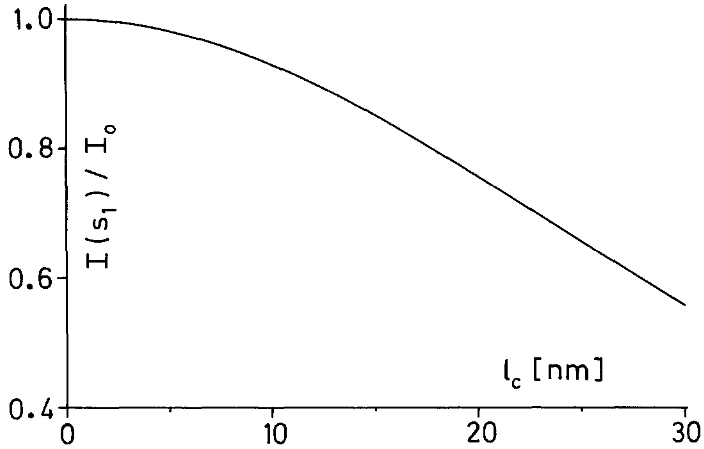

Fig. 5. The intensity of the first measured point $I(s_1)$ relative to the zero-intensity in the function of l_c (entrance slit 40 μm, the first measuring point was $s_1 = 8.84 \times 10^{-3}\,\text{nm}^{-1}$)

Therefore, for practical reasons it is necessary to note some other methods to find out the zero angle intensity or the parameter l_c:

(a) An approximated value of I_0 is given by the tentative extrapolation of the plot $\log I(s)$ vs. $\log s$, since on this plot the slope in the region of the first measured points is very small.

Another approximation is to calculate the deviation of the intensity of the first measured point s_1 relative to the zero intensity versus l_c for a given entrance slit (Fig. 5). In both cases the accuracy of the extrapolation depends on the coordinate of the first measured points ($\simeq$ the width of the entrance slit) and on the estimation of the parameter l_c. A theoretically exact method is given for the determination of l_c by the classical evaluation of the moments M_1 and M_2 of the scattering curve (Table 2). We have $M_1/M_2 = 2b/\pi$. The uncertainties due to the innermost – not measured, only extrapolated – part of the experimental curve, which can only be estimated by the evaluation, are minimized because $s \to 0$, and the quotient of the moments is formed.

(b) An exact, but more laborious method is to evaluate the radius of gyration R_q from the Guinier-plot of the "cross-section scattering curve" ($I_q(s) = sI(s)$) and/or R_d from the "thickness scattering curve" ($I_d(s) = s^2 I(s)$). The Eqs. (7) furnish l_c, and I_0 can be calculated e.g. from Eq. (5a). We can also utilize the ordinate-intercepts of the Guinier plots and calculate l_c from (12) and I_0 from Eq. (11a) or (11b).

(c) Finally it is to remark that often the Porod tail can be determined with great accuracy. We can utilize the first moment M_1 and the Porod constant K_P of the measured scattering curve (or M_1 and K_P from the smeared intensity curve) for the determination of I_0: the multiplication of (17) with the evaluated M_1 gives

$$(1/2)I_0^{1/n} = K_P^{-1/n} M_1 = tM_1.$$

For $n = 3/2$ (smeared scattering curve) the factor 1/2 is cancelled.

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