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SMALL-ANGLE X-RAY SCATTERING FROM SPHERICAL PARTICLES OF NON-UNIFORM ELECTRON DENSITY — ELECTRON DENSITY TRANSITION IS GRADUAL, OR PARTLY GRADUAL AND PARTLY SHARP*)

K. KRANJC

Institute of Physics of the University, Zagreb

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Abstract: The scattering curves for various models of spherical particles of non-uniform electron density were calculated and compared with scattering curves for homogeneous particles. Simple asymptotic laws were found for average intensities which show h^{-n} dependence, where h is proportional to the scattering angle. Whenever the electron density transition is sharp, or partly gradual and partly sharp, the exponent n is 4 regardless whether the sharp transition is at the edge of or inside the particle. If the whole electron density transition is gradual, n is greater than 4; $n = 6$ if the transition is linear, and $n = 8$ if the transition can be described by a cosine function.

1. Introduction

The small-angle X-ray scattering technique is often used to determine the shape and size both of great molecules, or micelles in dilute solutions, and of clusters or inclusions in solid materials. The angular distribution of the intensity of scattered rays has been calculated both for a number of particles of various shape but of uniform electron density and for some special distributions of electron density within the particle[1,2].

The scattering from spherical particles with a gradual decrease of electron density from the centre of the particle has recently been calculated[3]. The scattering

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curves were calculated for the electron density distributions described by the cosine and the Gaussian functions. In the first case the scattering curve at the large angles of the small-angle region oscillates round a curve which runs proportionally to $(2\Theta)^{-8}$, where 2Θ is the scattering angle. If the electron density transition from the centre of the particle outward is linear, the asymptotic behaviour is according to $(2\Theta)^{-6}$. Thus the gradual decrease of electron density, beginning at the centre of the particle, gives rise to a steeper decrease of intensity with the increasing scattering angle than does the sharp decrease of electron density in homogeneous particles in which case Porod's $(2\Theta)^{-4}$ law applies.

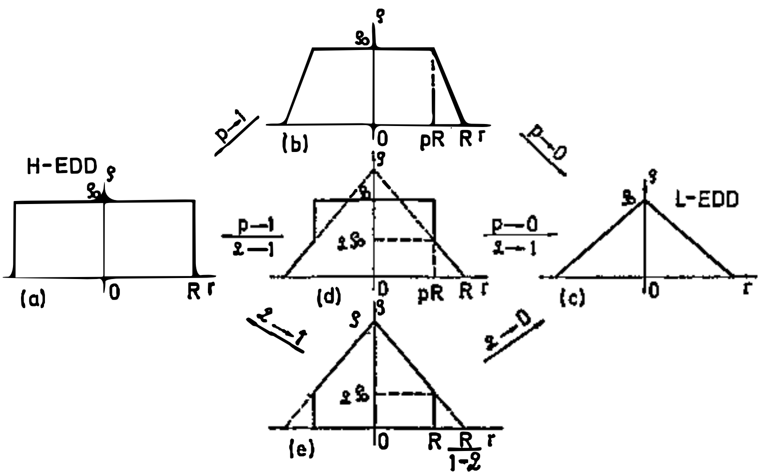

Fig. 1. Models of particles with linear electron density distribution: (b) L-A, (d) L-B1 and (e) L-B2 models, and their limiting cases: (a) homogeneous sphere (H-EDD particle), and (c) L--EDD particle.

In this paper the model of the gradual decrease of electron density from the centre of the particle will be modified in two ways to include more general cases. In model A the gradual decrease of electron density is restricted to the outer shell of the particle. Model B differs from model A in that the decrease of electron density is partly sharp. The scattering curves for particles represented by models A and B will be given, for three different shapes of electron density distribution: linear, cosine and Gaussian.

2. *Theory of scattering from spherically symmetric particles*

The amplitude of rays scattered from a spherical particle at the scattering angle 2Θ is

$$A(h) = A_e F(h) = A_e n \Phi(hR) = A_e \langle \varrho \rangle V \Phi(hR), \tag{1}$$

where $h = 4\pi \sin \Theta/\lambda$; in the small angle region, h is proportional to the scattering angle 2Θ. A_e is the amplitude scattered from a single electron, and n the excess or the deficit of the number of electrons with respect to the surrounding medium in volume V occupied by the particle of radius R. $\Phi(hR)$ is the amplitude normalized to unity for the zero scattering angle; $\langle\varrho\rangle$ is the average electron density which is presented by the function $\varrho(r)$; the electron density of the surrounding medium is supposed to be zero.

For spherical particles the scattering amplitude is given by

$$F(h) = \int_0^R 4\pi r^2 \varrho(r) \frac{\sin(hr)}{hr} \, dr \tag{2}$$

and

$$\Phi(hR) = \frac{\int_0^R 4\pi r^2 \varrho(r) \frac{\sin(hr)}{hr} \, dr}{\int_0^R 4\pi r^2 \varrho(r) \, dr}. \tag{3}$$

The denominator in (3) is related to the average electron density by

$$\langle\varrho\rangle = \frac{\int_0^R 4\pi r^2 \varrho(r) \, dr}{V} \tag{4}$$

and the mean square of the electron density is defined by

$$\langle\varrho^2\rangle = \frac{\int_0^R 4\pi r^2 \varrho^2(r) \, dr}{V}. \tag{5}$$

The angular dependence of the intensity of the radiation scattered from a spherical particle in electron units (I_{eu}), or absolute intensity, is given by

$$I_{eu} = \frac{I(h)}{I_e} = F^2(h) = \langle\varrho\rangle^2 V^2 \Phi^2(hR), \tag{6}$$

where $\Phi^2(hR)$ is the normalized intensity, i. e. the intensity scattered by a single electron of the particle.

The particle scattering has the following general features[1]:

— for zero scattering angle

$$I_{eu}(0) = F^2(0) = V^2 \langle \varrho \rangle^2; \tag{7}$$

— at small h, the first two terms representing the scattered intensity when developed as a power series are

$$\Phi^2(h) = 1 - \frac{(hR_g)^2}{3} + \ldots, \tag{8}$$

(Guinier approximation), where R_g is the radius of gyration defined *by*

$$R_g^2 = \frac{\int_0^R r^4 \varrho(r)\, dr}{\int_0^R r^2 \varrho(r)\, dr}; \tag{9}$$

— at large h, if Porod's law is valid, i. e. if the average intensity in the tail of the scattering curves runs proportinally to h^{-4}, we have

$$\lim_{h \to \infty} h^4 \langle I_{eu}(h) \rangle = 2\pi (\Delta \varrho)^2 S, \tag{10}$$

where S is the surface of the particle, and $\Delta\varrho = \varrho$ in the case of a particle with uniform electron density ϱ immersed in a medium of zero density; and

— the overall scattering in the reciprocal space depends on the average square of electron density

$$\int_0^\infty h^2 F^2(h)\, dh = 2\pi^2 \langle \varrho^2 \rangle V. \tag{11}$$

3. Results of calculation for different models of electron density distribution

The middle columns of Figs. 1,4 and 7 show all models of particles for which the scattering curves were studied, each model showing electron density profiles across one diameter. The electron density (e. d.) decreases according to the linear (Fig. 1), the cosine (Fig. 4) or the Gaussian function (Fig. 7). On the right sides of Figs. 1,4 and 7 the limiting cases are shown, where the e. d. decrease starts at the centre of the particle. The model on the left side is a homogeneous sphere. For these particles we shall use abbreviated symbols: H-EDD for uniform e. d. (homogeneous sphere), and analogously L-EDD, Cos-EDD and Gauss-EDD particles if they have the linear, the cosine or the Gaussian e. d. distribution.

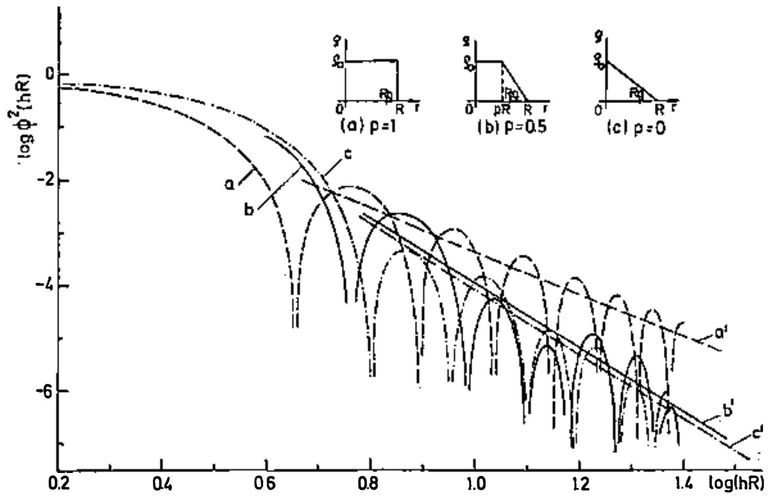

Fig. 2. Comparison of the scattering curve b of model L-A with the scattering curves of the H-EDD particle (curve a) and the L-EDD particle (curve c.) Note the steeper course of asymptotes b′ and c′ in comparison to a′, due to the gradual transition of electron density.

Symbol A will indicate that the decrease of e. d. is continuous and limited to the outer shell of the particle, and thus we shall distinguish models L-A (Fig. 1b), Cos-A (Fig. 4b) and Gauss-A (Fig. 7b). Symbol B will be used to indicate the existence of a sharp transition of e. d. As this transition may occur either within the particle or on its edge, we must distinguish two B models, — B1 and B2. Thus we have L-B1, L-B2 (Figs. 1d, 1e), Cos-B1, Cos-B2 (Figs. 4d, 4e) and Gauss-B1, Gauss-B2 (Figs. 7d, 7e) models.

In the case of particles with a finite radius (L-and Cos-particles) the radius will be denoted by R, and the radius at which a change in the character of e. d. distribution occurs, with pR. Parameter p is then restricted to $0 \leq p \leq 1$; with $p = 1$ we have a homogeneous sphere, and $p = 0$ holds for L-EDD and Cos--EDD particles.

Particles whose inhomogeneity of e. d. can be described by a linear function which decreases in the direction of the edge of the particle, will be described in greater detail than the other, because the scattering functions are simple but still contain all the characteristic features due to inhomogeneity.

Particles with linear electron density distribution:

— Model L-A (Fig. 1b). The e. d. is defined as

$$\begin{aligned} \varrho(r) &= \varrho_0 && \text{for} \quad 0 \le r \le pR, \\ \varrho(r) &= \frac{\varrho_0}{1-p}\left(1 - \frac{r}{R}\right) && \text{for} \quad pR \le r \le R, \\ \varrho(r) &= 0 && \text{for} \quad r \ge R. \end{aligned} \tag{12}$$

The normalized amplitude, calculated by help of relation (3) is given by

$$\Phi(hR, p) = \frac{12}{p^4 - 1} \cdot \frac{1}{(hR)^4} \{hR[\sin(hR) - p\sin(phR)] + 2[\cos(hR) - \cos(phR)]\}. \tag{13}$$

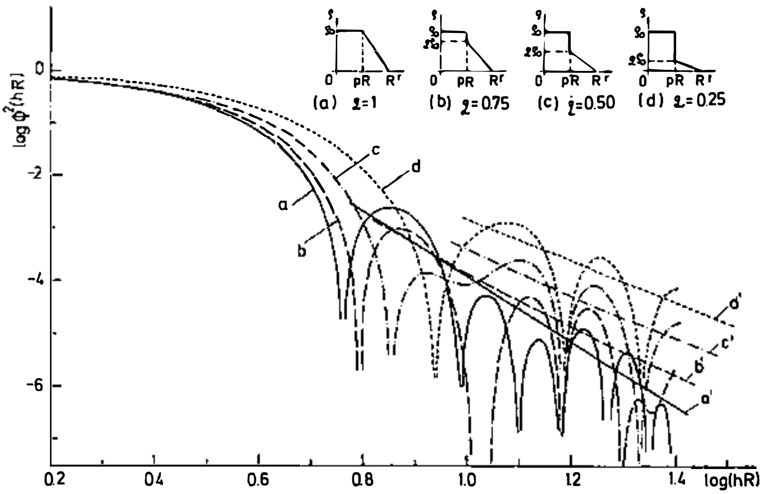

Fig. 3. Influence of the height of the abrupt drop of electron density on the shape of scattering curves (L-B1 models). Curve a is the scattering curve of the L-A particle shown in Fig. 2.

The average electron density obtained by relation (4) is

$$\langle\varrho\rangle = \frac{\varrho_0}{4}(1+p)(1+p^2) \tag{14}$$

and the average square of electron density given by (5) is

$$\langle\varrho^2\rangle = \varrho_0^2 \cdot \frac{1}{10}(1 + 2p + 3p^2 + 4p^3). \tag{15}$$

The radius of gyration as calculated by (9) is

$$R_g^2 = R^2 \cdot \frac{2}{5}\left(1 + \frac{p^4}{1+p^2}\right). \tag{16}$$

By squaring Equ. (13), we obtain the normalized intensity Φ^2. Multiplying this function by the square of the number of excess or deficit electrons in the particle with respect to the surrounding medium, the true scattering function in the electron units would be obtained.

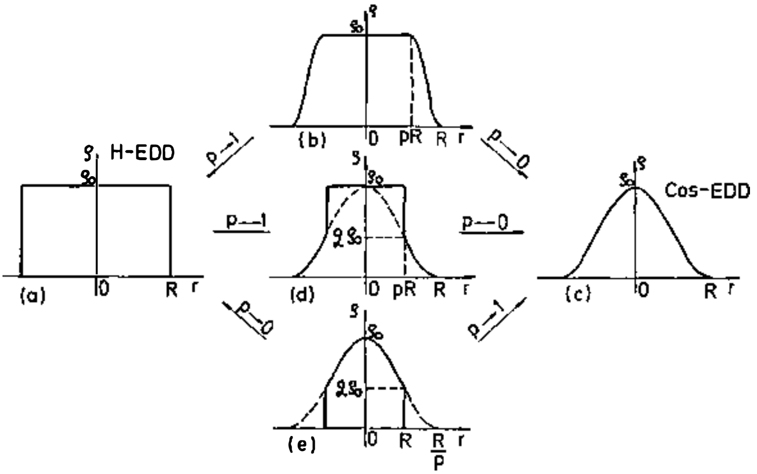

Fig. 4. Models of particles with cosine distribution of electron density: (b) Cos-A, (d) Cos-B1 and (e) Cos-Be models, and the limiting cases: (a) H-EDD particle, and (c) Cos-EDD particle.

In order to see the asymptotic behaviour of the average intensities at great angles, the oscillating sine and cosine terms in function Φ^2 must be averaged. Function I_{as} which was obtained in this manner, is

$$I_{as}(hR, p) = \frac{72}{(1-p^4)^2}\left[\frac{1+p^4}{(hR)^6} + \frac{8}{(hR)^8}\right]. \tag{17}$$

We shall call such functions »analytical« asymptotes.

— H-EDD particle (Fig. 1a). Inserting $p = 1$ in relations (13) to (16), we obtain the well known relations for the homogeneous sphere

$$\Phi(hR) = \frac{3}{(hR)^3}[\sin(hR) - hR\cos(hR)] \tag{18}$$

$$\langle\varrho\rangle = \varrho_0; \quad \langle\varrho^2\rangle = \varrho_0^2; \quad R_g^2 = R^2 \cdot \frac{3}{5}. \tag{19}$$

However, the asymptote cannot be obtained directly from relation (17), because the average values of certain trigonometric terms depend on the value of p. We shall point out those terms in which there is a difference in the average values, if $p = 1$

$$\langle \sin(hR) \sin(phR) \rangle = \begin{cases} \frac{1}{2} & \text{for} \quad p = 1 \\ 0 & \text{for} \quad 0 \leq p < 1, \end{cases}$$
$$\langle \cos(hR) \cos(phR) \rangle = \begin{cases} \frac{1}{2} & \text{for} \quad p = 1 \\ 0 & \text{for} \quad 0 \leq p < 1. \end{cases} \tag{20}$$

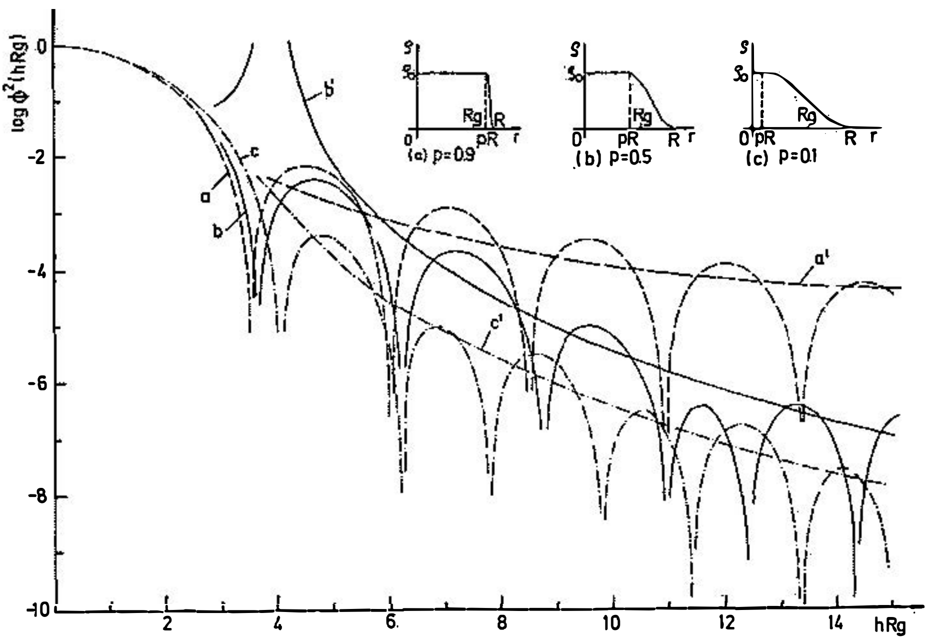

Fig. 5. Scattering curves a, b, c and their calculated asymptotes a′, b′, c′ of three Cos-A models (a), (b) and (c).

Using otherwise the same procedure as in the calculation of (17), we obtain the known asymptote for the homogeneous sphere

$$I_{as}(hR) = \frac{9}{2}\left[\frac{1}{(hR)^4} + \frac{1}{(hR)^6}\right]. \tag{21}$$

— L-EDD particle (Fig. 1c). With $p = 0$, we have

$$\Phi(hR) = \frac{12}{(hR)^4}[2 - hR\sin(hR) - 2\cos(hR)] \tag{22}$$

$$\langle \varrho \rangle = \frac{\varrho_0}{4}; \quad \langle \varrho^2 \rangle = \frac{\varrho_0^2}{10}; \quad R_g^2 = R^2 \cdot \frac{2}{5}. \tag{23}$$

In calculating the asymptote from (13) for $p = 0$ we must take into account that

$$\langle \sin^2 (phR) \rangle = \begin{matrix} 0 & \text{for} & p = 0 \\ \frac{1}{2} & \text{for} & 0 < p \leq 1 \end{matrix}$$

$$\langle \cos^2 (phR) \rangle = \begin{matrix} 1 & \text{for} & p = 0 \\ \frac{1}{2} & \text{for} & 0 < p \leq 1 \end{matrix} \tag{24}$$

and we obtain

$$I_{as}(hR) = 72 \left[\frac{1}{(hR)^6} + \frac{12}{(hR)^8} \right]. \tag{25}$$

— Model L-B1 (Fig. 1d). The electron density is presented by

$$\begin{aligned} \varrho(r) &= \varrho_0 && \text{for} \quad 0 \leq r \leq pR, \\ \varrho(r) &= \varrho_0 \frac{q}{1-p}\left(1 - \frac{r}{R}\right) && \text{for} \quad pR < r \leq R, \\ \varrho(r) &= 0 && \text{for} \quad r \geq R, \end{aligned} \tag{26}$$

with $0 \leq p \leq 1$ and $0 \leq q \leq 1$.

With $z = hR$, we obtain the following formulae

$$\Phi(z, p, q) = \frac{12}{(1-p)[4p^3 + q(1 + p + p^2 - 3p^3)} \cdot \frac{1}{z^4} \{1 - q z \sin z - 2 q \cos z +$$
$$+ (1 - p - q + 2pq) z \sin(pz) - [pz^2(1-p)(1-q) - 2q] \cos(pz)\}, \tag{27}$$

$$\langle \varrho \rangle = \varrho_0 \left[p^3 + \frac{p}{4}(1 + p + p^2 - 3p^3) \right], \tag{28}$$

$$\langle \varrho^2 \rangle = \varrho_0^2 \left[p^3 + \frac{q^2}{10}(-6p^3 + 3p^2 + 2p + 1) \right], \tag{29}$$

$$R_g^2 = R^2 \cdot \frac{2}{5} \cdot \frac{6p^5(1-p) + 6q(1-p^5) - 5q(1-p^6)}{4p^3(1-p) + 4q(1-p^3) - 3q(1-p^4)}, \tag{30}$$

$$I_{as} = \left[\frac{3p(1-q)}{4p^3 + q(1 + p + p^2 - 3p^3)} \right]^2 \left[\frac{1}{z^4} + \frac{(1-p)^2 + 2q(q + p - 1)}{p^2(1-p)^2(1-q)^2} \cdot \frac{1}{z^6} + \right.$$
$$\left. + \frac{8q^2}{p^2(1-p)^2(1-q)^2} \cdot \frac{1}{z^8} \right]. \tag{31}$$

Inserting $q = 1$ in equations (27) to (31), we obtain formulae (13) to (17), representing the L-A particle shown in Fig. 1b.

— Model L-B2 (Fig. 1e). The e. d. distribution is defined as

$$\varrho(r) = \varrho_0 \left[1 - \frac{(1-q)\,r}{R}\right] \quad \text{for} \quad 0 \le r \le R,$$
$$\varrho(r) = 0 \quad \text{for} \quad r > R. \tag{32}$$

If $z = hR$, the scattering amplitude, the radius of gyration and the asymptote are

$$\Phi(z,q) = \frac{12}{1+3q} \cdot \frac{1}{z^4}\{2(1-q) + (2q-1)\,z\sin z - [2(1-q) + q\,z^2]\cos z\}, \tag{33}$$

$$R_g^2 = R^2 \cdot \frac{2}{5} \cdot \frac{1+5q}{1+3q}, \tag{34}$$

$$I_{as}(z,q) = \frac{72\,q^2}{(1+3q)^2}\left[\frac{1}{z^4} + \frac{1}{q^2} \cdot \frac{1}{z^6} + \frac{12(1-q)^2}{q^2} \cdot \frac{1}{z^8}\right]. \tag{35}$$

In Fig. 2 the scattering curve of one particle belonging to the model L-A is presented in order to compare it with the scattering curves of the H-EDD and L-EDD particles. In Fig. 3 three cases of model L-B1 are compared with model L-A showing the influence of the abrupt drop in electron density inside the particle.

The electron density decrease in the particle has the form of a cosine function:

— Model Cos-A (Fig. 4b). E. d. is defined as

$$\varrho(r) = \varrho_0 \quad \text{for} \quad 0 \le r \le pR,$$
$$\varrho(r) = \frac{\varrho_0}{2}\left[1 + \cos\frac{\pi(r-pR)}{R(1-p)}\right] \quad \text{for} \quad pR \le r \le R, \tag{36}$$
$$\varrho(r) = 0 \quad \text{for} \quad r \ge R.$$

The normalized scattering amplitude as a function of $z = hR$, the average electron density and the radius of gyration are given by

$$\Phi(z,p) = \frac{3\pi^4}{\pi^2(1+p^3) - 6(1-p)^2(1+p)} \cdot \frac{1}{z^3[\pi^2 - z^2(1-p)^2]}$$
$$\cdot \left\{\frac{\pi^2 - 3z^2(1-p)^2}{\pi^2 - z^2(1-p^2)}[\sin z + \sin(pz)] - z[\cos z + p\cos(pz)]\right\}, \tag{37}$$

$$\langle\varrho\rangle = \varrho_0 \left[\frac{1+p^3}{2} - \frac{3(1-p^2)(1+p)}{\pi^2}\right], \quad (38)$$

$$R_g^2 = R^2 \cdot \frac{3}{5\pi^2} \cdot$$

$$\cdot \frac{(\pi^4-20\pi^2+120)(p^4+1)+(\pi^4-60\pi^2+480)p(p^2+1)+(\pi^4-80\pi^2+720)p^2}{(\pi^2-6)(1+p^2)+(12-\pi^2)p}. \quad (39)$$

The asymptote in complete form is

$$I_{as}(z,p) = \frac{9\pi^8}{2[\pi^2(1+p^3)-6(1-p)^2(1+p)]^2} \cdot \frac{1}{[\pi^2-z^2(1-p)^2]^4} \cdot$$

$$\cdot \left[\frac{2\pi^4}{z^6} + \frac{\pi^4(1+p^2)-12\pi^2(1-p)^2}{z^4} + \frac{18(1-p)^4-2\pi^2(1-p)^2(1+p)^2}{z^2} + \right.$$

$$\left. + (1-p)^4(1+p^2)\right], \quad (40)$$

and in the usual form, showing h^{-n} dependence,

$$I_{as}(z,p) = \frac{9\pi^8(1+p^2)}{2[\pi^2(1+p^3)-6(1-p)^3]^2(1-p)^4}\left[\frac{1}{z^8} + \right.$$

$$\left. + \frac{18(1-p)^2+2\pi^2(1+p^2)}{(1-p)^2(1+p^2)} \cdot \frac{1}{z^{10}} + \ldots\right]. \quad (40a)$$

Cos-EDD particle (Fig. 4c). If we insert $p = 0$ into equations (37) to (39), we obtain equations which are identical to those in the previous paper[3]. In calculating the asymptote, we had to derive it from (37), taking into account the averages given in (24). The formulae for the Cos-EDD particle in the present notation are

$$\Phi(z) = \frac{3\pi^4}{(\pi^2-6)(\pi^2-z^2)^2 z^3}[(\pi^2-3z^2)\sin z - z(\pi^2-z^2)\cos z], \quad (41)$$

$$\langle\varrho\rangle = \varrho_0 \frac{\pi^2-6}{2\pi^2}, \quad (42)$$

$$R_g^2 = R^2 \cdot \frac{3}{5} \cdot \frac{\pi^4-20\pi^2+120}{\pi^2(\pi^2-6)}, \quad (43)$$

$$I_{as}(z) = \frac{9\pi^8}{2(\pi^2-6)^2(\pi^2-z^2)^4}\left[\frac{\pi^4}{z^6} + \frac{\pi^2(\pi^2-6)}{z^4} + \frac{9-2\pi^2}{z^2} + 1\right]. \quad (44)$$

If $p = 1$, from formulae (37) to (39) we obtain formulae which describe the H-EDD particle.

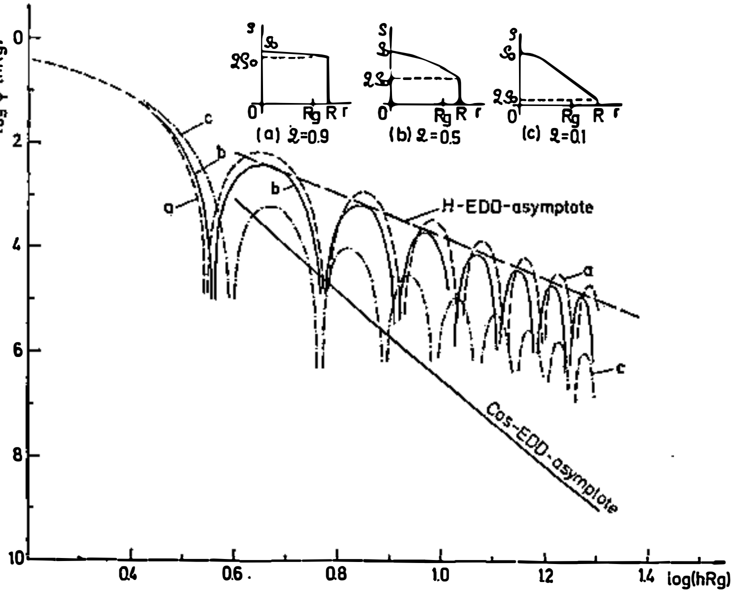

Fig. 6. Scattering curves of Cos-B2 models. Note the regular arrangement of peaks. The presence of the abrupt drop of electron density at the edge of the particle diminishes the slope of the asymptotes in comparison to that of the pure Cos-EDD particle.

— Model Cos-B1 (Fig. 4d). The model considered here is not so general as the linear model shown in Fig. 1d; in order to obtain more simple formulae, the independent parameter q was not included. In our case, q is related to p by $q = [1 + \cos(p\pi)]/2$. Thus the e. d. distribution is

$$\begin{aligned} \varrho(r) &= \varrho_0 && \text{for} \quad 0 \leq r \leq pR, \\ \varrho(r) &= \frac{\varrho_0}{2}\left(1 + \cos\frac{\pi r}{R}\right) && \text{for} \quad pR < r \leq R, \\ \varrho(r) &= 0 && \text{for} \quad r \geq R. \end{aligned} \tag{45}$$

With $z = hR$, the normalized amplitude is

$$\Phi(z, p) = \frac{3\pi^3}{F(p) z^3 (\pi^2 - z^2)^2}\Big[f_1(z)\sin z - f_2(z)\cos z + f_3(z, p)\sin(pz) - - f_4(z, p)\cos(pz)\Big], \tag{46}$$

where

$$F(p) = \pi^3 (p^3 + 1) - 3 (p^2\pi^2 - 2) \sin (p\pi) - 6\pi [1 + p \cos (p\pi)],$$

$$f_1(z) = \pi^2 (\pi^2 - 3z^2),$$

$$f_2(z) = \pi^2 z (\pi^2 - z^2),$$

$$f_3(z, p) = (\pi^2 - z^2)^2 - z^2 (\pi^2 + z^2) \cos (p\pi) - p\pi z^2 (\pi^2 - z^2) \sin (p\pi),$$

$$f_4(z\, p) = z [p (\pi^2 - z^2)^2 - 2\pi z^2 \sin (p\pi) + pz^2 (\pi^2 - z^2) \cos (p\pi)].$$

$$\langle \varrho \rangle = \varrho_0 \frac{1}{2\pi^3} \{\pi^3 (1 + p^3) + 3 (p^2\pi^2 - 2) \sin (p\pi) - 6\pi [1 + p \cos (p\pi)]\}, \quad (47)$$

$$R_g^2 = R^2 \cdot \frac{3}{5\pi^2} \cdot$$

$$\cdot \frac{\pi^5(1+p^5)+20\pi(6-\pi^2)-5(p^4\pi^4-12p^2\pi^2+24)\sin(p\pi)-20p\pi(p^2\pi^2-6)\cos(p\pi)}{\pi^3 (1+p^3) - 6\pi - 3 (p^2\pi^2 - 2) \sin (p\pi) - 6p\pi \cos (p\pi)}, \quad (48)$$

$$I_{as}(z, p) = \frac{1}{2} \left[\frac{3\pi^3}{F(p) z^3 (\pi^2 - z^2)^2}\right]^2 [f_1^2(z) + f_2^2(z) + f_3^2(z, p) + f_4^2(z, p)]. \quad (49)$$

With $p = 0$, formulae for the Cos-EDD particle will be obtained, while $p = 1$ gives formulae for the H-EDD particle.

— Model Cos-B2 (Fig. 4e). E. d. distribution is given by

$$\varrho(r) = \frac{\varrho_0}{2} \left[1 + \cos \frac{p\pi r}{R}\right] \quad \text{for} \quad 0 \le r \le R,$$

$$\varrho(r) = 0 \quad \text{for} \quad r > R. \quad (50)$$

Parameters q and p are related by $q = [1 + \cos (p\,\pi)]/2$. With $p\,\pi = \beta$ and $hR = z$ we have

$$\Phi(z, \beta) = \frac{3\beta^3}{\beta^3 + 6\beta \cos \beta + 3 (\beta^2 - 2) \sin \beta} \cdot$$

$$\cdot \frac{1}{z^3 (z^2 - \beta^2)^2} \{[(z^2 - \beta^2)^2 - \beta z^2 (z^2 - \beta^2) \sin \beta + \quad (51)$$

$$+ z^2 (z^2 + \beta^2) \cos \beta] \sin z - [z(z^2 - \beta^2)^2 + 2\beta z^3 \sin \beta + z^3 (z^2 - \beta^2) \cos \beta] \cos z\},$$

$$R_g^2 = R^2 \frac{3}{5\beta^2} \cdot \frac{\beta^5 + 5 (\beta^4 - 12\beta^2 + 24) \sin \beta + 20\beta (\beta^2 - 6) \cos \beta}{\beta^3 + 3 (\beta^2 - 2) \sin \beta + 6\beta \cos \beta}. \quad (52)$$

The asymptote is equal to one half of the factors in front of the bracket multiplied by the sum of squares of coefficients of the sine and cosine functions.

For $p = 1$ ($\beta = \pi$) we obtain the Cos-EDD case, and for $p = 0$ the H-EDD case.

Fig. 5 presents the scattering curves of some Cos-A models, and Fig. 6 the influence of the abrupt drop of electron density at the edge of the particle on scattering curves (Cos-B2 model).

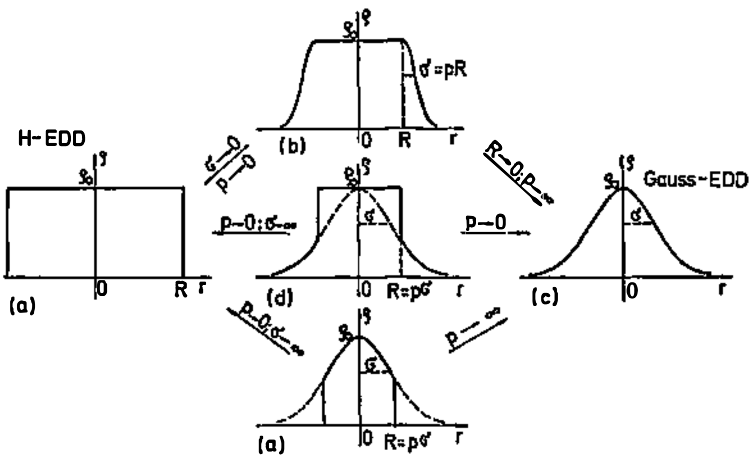

Fig. 7. Models of particles with the Gaussian distribution of electron density: (b) Gauss-A, (d) Gauss-B1 and (e) Gauss-B2 models, and the limiting cases: (a) H-EDD particle and (c) Gauss -EDD particle.

The electron density decrease is a Gaussian curve:

— Model Gauss-A (Fig. 7b). Since this particle has no finite boundaries, we denote with R the radius at which a change in the e. d. distribution function takes place. With $p > 0$, and $\sigma = pR$, e. d. distribution is defined as

$$\varrho(r) = \varrho_0 \quad \text{for} \quad 0 \leq r \leq R,$$

$$\varrho(r) = \varrho_0 \exp\left[-\frac{(r-R)^2}{2\sigma^2}\right] = \varrho_0 \exp\left[-\frac{(r-R)^2}{2p^2R^2}\right] \quad \text{for} \quad R \leq r \leq \infty. \tag{53}$$

With $z = hR$, the normalized scattering amplitude is

$$\Phi(z, p) = \frac{3}{2 + 3p(\sqrt{2\pi} + 4p) + 3\sqrt{2\pi}\, p^3} \cdot \frac{1}{z^3}\left\{\left[2 + 2p^2z^2 + (\sqrt{2\pi}\, pz^2 - \right.\right.$$

$$- 2Ap^4z^4)\exp\left(-\frac{p^2z^2}{2}\right)\Bigg]\sin z + \tag{54}$$

$$+ \left[-2z + \left(\sqrt{2\pi}\,p^3z^3 + 2A\,p^2z^3\right)\exp\left(-\frac{p^2z^2}{2}\right)\right]\cos z\Bigg\},$$

where $A = \sum_{n=0}^{\infty} \frac{1}{2n+1} \cdot \frac{(pz)^{2n}}{2^n\,n!}$.

As the volume of the particle is infinite, the average e. d. is zero, but the product of the average e. d. and the volume, or the number of electrons in the particle (the square of which determines the zero angle intensity as seen in relation (7)) is

$$\langle\varrho\rangle\,V = \varrho_0\,R^3\frac{2\pi}{3}(2 + 3\sqrt{2\pi}\,p + 12\,p^2 + 3\sqrt{2\pi}\,p^3). \tag{55}$$

The radius of gyration is

$$R_g^2 = R^2\,\frac{3}{5}\cdot\frac{2\,(1 + 20p^2 + 40p^4) + 5\sqrt{2\pi}\,p\,(1 + 6\,p^2 + 3p^4)}{2\,(1 + 6p^2) + 3\sqrt{2\pi}\,p\,(1 + p^2)}. \tag{56}$$

The course of the asymptote, i. e. the average intensity at greater scattering angles, was studied graphically.

With $p = 0$, we obtain formulae for the H-EDD particle.

Gauss-EDD particle (Fig. 7c). The other extreme case of the Gauss-A model is a »particle« in which the whole course of the e. d. is Gaussian. This particle was studied previously[3]. The same formulae can be obtained from (54) to (56) if we put $R = 0$, $p = \infty$, but $pR = \sigma \neq 0$. Thus, if m and n are integers and $m > n$, we have $p^nz^m = 0$, $(pz)^n \neq 0$, and $p^nR^m = 0$, $(pR)^n \neq 0$,

$$\Phi^2\,(h) = \exp\,(-h^2\sigma^2), \tag{57}$$

$$\langle\varrho\rangle V = \varrho_0\sigma^3\,(2\pi)^{\frac{3}{2}},\quad R_g^2 = 3\sigma^2. \tag{58}$$

— Model Gauss-B1 (Fig. 7d). A sharp transition occurs at $r = R$. We introduce the parameter $p > 0$ so that $R = p\sigma$. The e. d. is given by

$$\begin{aligned} \varrho\,(r) &= \varrho_0 && \text{for} \quad 0 \leq r \leq p\,\sigma, \\ \varrho\,(r) &= \varrho_0\exp\left(-\frac{r^2}{2\sigma^2}\right) && \text{for} \quad p\,\sigma < r \leq \infty. \end{aligned} \tag{59}$$

— Model Gauss B2 (Fig. 7e). A sharp transition is at the edge of the particle, at $R = p\sigma$, with $p > 0$. The e. d. varies as

$$\varrho(r) = \varrho_0 \exp\left(-\frac{r^2}{2\sigma^2}\right) \qquad \text{for} \qquad 0 \leq r \leq p\sigma,$$

$$\varrho(r) = 0 \qquad \text{for} \qquad p\sigma < r \leq \infty. \tag{60}$$

The scattering for both Gauss-B models was calculated by numerical integration and the general features of scattering curves studied graphically.

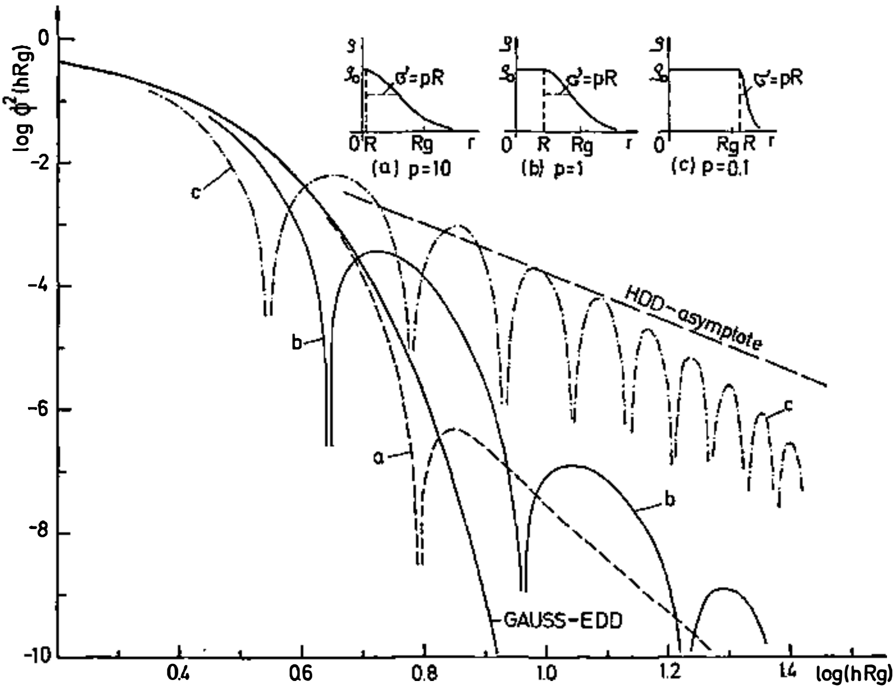

Fig. 8. Scattering curves of three Gauss-A models. It can be seen that the smaller is the parameter p, the larger are the angles at which the steep course of the average intensitites is attained. The full line is the scattering curve of the Gauss-EDD particle.

In Fig. 8 three examples of Gauss-A models are presented, while in Fig. 9 can be seen the characteristic features of the scattering curves when an abrupt drop occurs inside the particle.

4. *Discussion of the shapes of scattering curves for different models*

General comment on the scattering curves. Many features found in the scattering curves of homogeneous particles appear in the scattering curves of particles with non-uniform electron density.

For all scattering functions of finite particles the general features known as Guinier approximation and invariant and given by relations (8) and (11) could be proved analytically. The Guinier approximation, i. e. the same course of the scattering curves at the smallest scattering angles for all particles of the same radii of gyration, can be seen in Figs. 5, 6, 8 and 9, where the intensity is presented as a function of hR_g. The angular region in which such a scattering curve follows the Gaussian curve is the larger, the more the electron density profile resembles the true Gaussian one (see, for instance, Fig.8). In the plots in which intensity is presented as a function of hR, the radius of gyration is the larger, the steeper is the course of the curve at small angles. In Fig. 2, for instance, where the sizes of the radii of gyration are indicated in the profiles of electron density of the corresponding particles, it can be seen that of the three models the homogeneous sphere has the largest R_g.

Only one of the scattering curves is monotonous, i. e. without the subsidiary maxima. This curve belongs to the Gauss-EDD particle (model Fig. 7c, relation (57), curves denoted by Gauss-EDD in Figs. 8 and 9). Such scattering is possible only if the electron density distribution is given by a single function from the centre of the particle to infinity. In the case of the Gaussian distribution of electron density the scattering function is again a Gaussian function. When even a small part of the particle is, for instance, homogeneous, as in model (a) in Fig. 8, the scattering has at least one subsidiary maximum like curve *a* in the same figure. The reason for the oscillations in the scattering curves is that the radii R_t at which the electron density distribution changes its course, enter, as limits of integration, formula (2) (which was used for calculating the amplitude) and appear in the scattering functions as arguments hR_t in the sine and cosine functions. Now we have scattering curves where only one argument, hR, appears, and others with sine and cosine terms of both hR and phR. The presence of terms containing sine and cosine of phR in the scattering curves of the L-A, Cos-A, L-B1 and Cos-B1 models is the reason why the peaks of the subsidiary maxima do not decrease monotonously with the increasing scattering angle or have a very irregular arrangement (see, for instance, curve *b* in Fig. 2 and some of the curves in Figs. 3 and 5).

The minima in the scattering curves reach zero intensity values. This is not the case with the scattering curves of homogeneous particles which are not spherical.

By averaging the sine and cosine terms appearing in the scattering functions we obtained the expressions for the curves which should show the course of the average intensities. However, two remarks concerning these expressions should be made. First, the calculated »analytical« asymptotes cannot represent properly the average intensities if the peaks are distributed irregularly. In this case the »true« asymptote, i. e. the line which connects the half intensities of the maxima, is a zig-zag line. This line may consistently follow the analytical asymptote as in the case of the L-EDD particle (curve c and asymptote c' in Fig. 2), or roughly follow the asymptote as in the case of the L-A particle where $p = 0.5$ (curve b and asymptote b′ in Fig. 2).

The second remark is that for some values of parameter p the mathematical expressions for the L-A and Cos-A asymptotes do not give the correct course of the scattering curves. In the case of L-A models the analytical asymptotes, as calculated by relation (17) for different p, are all nearly parallel to lines b′ and c′ in Fig. 2, whereas the scattering curves gradually change their course from curve a (Fig. 2) to the steeper course of curve c as p goes from 1 to 0. The reason for not showing the proper trend when p is greater than about 0.7 lies in the procedure used to obtain the analytical asymptotes: the averages of all simple sine and cosine functions were taken as zero regardless of the arguments of these functions.

There is another reason for the inadequacy of the asymptote for the Cos-A particle. As seen in Equ. (40), the asymptote has a pol at $hR = \pi/(1 - p)$ where the value rises to infinity (see curve b′ in Fig. 5). However, excluding the angular range where the trend of the asymptote is meaningless, the remaining parts follow the trend of scattering curves quite well.

For other models the analytical asymptotes correctly describe the asymptotic behaviour of the scattering functions throughout the angular range, but for all models they show correctly the asymptotic behaviour at sufficiently great scattering angles.

Asymptotic behaviour of scattering curves. It is well known that the scattering curves of homogenous particles oscillate round a curve which runs proportionally to h^{-4} (Porod's law). Studying the relations for the asymptotes for different models we can see that here too a simple asymptotic law applies: the average intensity at sufficiently great angles becomes proportional to h^{-n}. However, the value of n makes a striking difference between the A and B models. The exponent n is greater than 4 whenever the total decrease of electron density is gradual (model A). In the case of a linear decrease $n = 6$, and if the decrease is of the cosine type $n = 8$. For the model Gauss-A n is about 10.

However, the presence of an abrupt drop in electron density, either at the edge of the particle or inside the particle, gives rise to a term in the expression for the asymptote which is proportional to h^{-4}.

Most of the figures are presented in log-log plots to show the asymptotic behaviour of the average intensities. As can be seen in Fig. 2, the slope of the asymptote a′ belonging to the scattering curve a of the homogeneous sphere (a) is smaller than the slopes of other asymptotes, because of the three particles only this one has a sharp transition of electron density. In Fig. 3 asymptote a′ is steeper than all the other asymptotes because the corresponding particle (a) is the only one which has no sharp transition of electron density. The larger the drop in electron density, the smaller the angles at which the h^{-4} course would be reached. This can be seen in comparing the slopes of the asymptotes d′, c′ and b′ in Fig. 3. In

Fig. 6 we can see that due to the presence of the sharp transition of electron density the asymptotic behaviour of the scattering curves (Cos-B2 models) is similar to that of the homogeneous sphere. The most striking in this respect are the Gauss--B1 and -B2 models. If we compare Fig. 9 with Fig. 8, we shall see that even a small drop in electron density rises the slope in the log-log plot to −4.

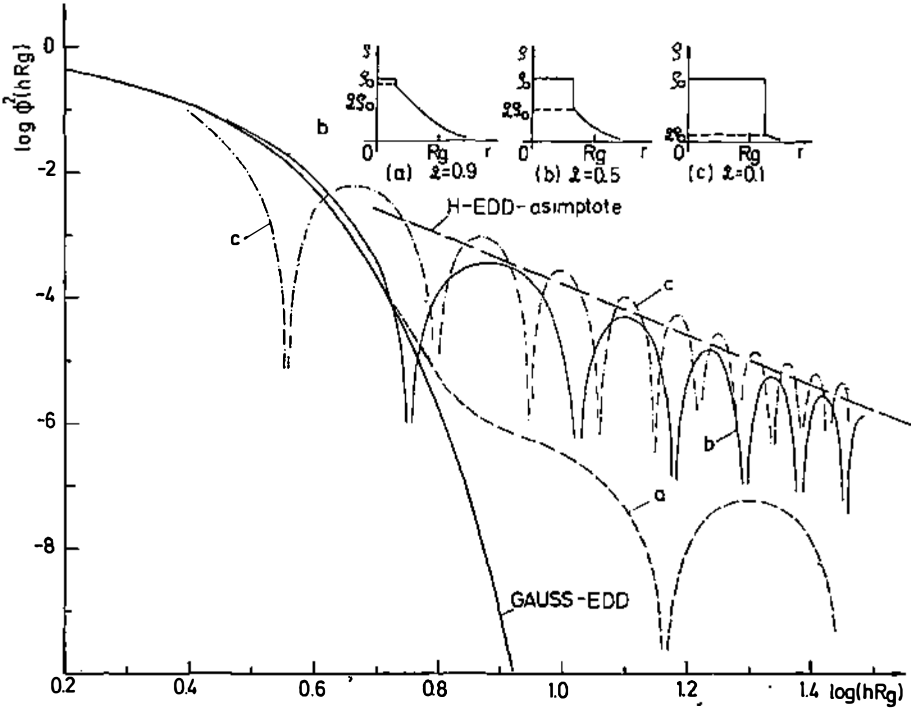

Fig. 9. Scattering curves of the Gauss-B1 models. Note the regular arrangement of the peaks, which run nearly parallel to the H-EDD asymptote. The full line is the scattering curve of the Gauss-EDD particle.

The meaning of Porod's law when the particles are not homogeneous. The well known Equ. (10) gives the relationship between the constant Porod product $h^4\langle I\rangle$ and the surface of the homogeneous particle. Now we have seen that the scattering curve which obeys Porod's law does not necessarily prove the existence of a homogeneous particle. The Porod product would be constant even in the case of an inhomogeneous particle if only a sharp transition of electron density is present. The question arises which features of the particle are inherent in the value of the Porod product. It will certainly not be the surface of the whole particle, because the h^{-4} law was proved also for »particles« with no finite boundaries (model B1 with the Gaussian electron density distribution).

To find the answer, we shall relate the constant Porod product on the left side of relation (10) to the functions which we have already calculated

$$\lim_{h\to\infty} h^4 \langle I_{eu}(h)\rangle = \lim_{h\to\infty} h^4 \langle\varrho\rangle^2 V^2 \langle\Phi^2(hR)\rangle = \lim_{h\to\infty} h^4 \langle\varrho\rangle^2 V^2 I_{as}.$$

Using the expressions obtained for $\langle\varrho\rangle$ or $\langle\varrho\rangle V$ and I_{as} for different models, the general result will be

$$\lim_{h\to\infty} h^4 \langle\varrho\rangle^2 V^2 I_{as} = 2\pi\, S_{1,2}\,(\Delta\varrho)^2_{1,2}, \tag{61}$$

where $S_{1,2}$ is the surface of the sphere, which ends just where the sharp transition of electron density occurs, and $(\Delta\,\varrho)_{1,2}$ is the difference of electron densities on both sides of this surface. The validity of relation (61) was also proved for the Gaussian electron density distribution for which the required functions were found by numerical integration.

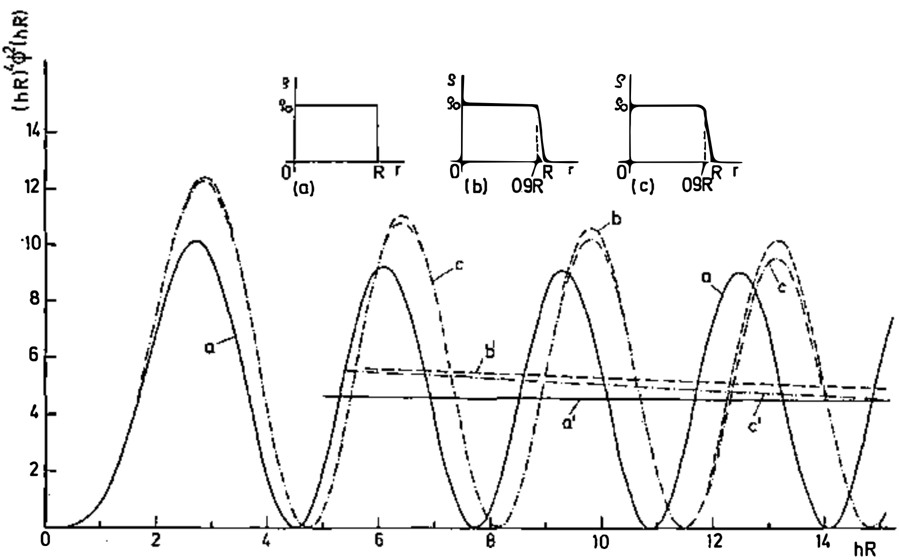

Fig. 10. Comparison of the scattering curves of L-A and Cos-A models, which have equal parameters p (0.9), with the scattering curve of a homogeneous sphere of the same radius.

Thus the meaning of the specific surface, which can be experimentally determined from the constant Porod product in the case of an ideal two-phase system (with the sharp electron density transition at the boundary of two homogeneous phases), has to be modified if one phase consists of inhomogeneous particles.

Finally, we shall compare the scattering curves of the L-A and Cos-A particles to see whether the manner in which the electron density decreases, has any major effect on the shape of scattering curves. If parameter p differs much from

1, the curves will differ rather strongly: neither is the location of maxima the same, nor are the intensities and irregularities in peak distribution similar. The slope of the asymptote of the Cos-A curve is smaller at small angles, becoming at large angles ($n = 8$) greater than that of the L-A particle ($n = 6$). For greater p, however, i. e. when the electron density transition occurs only in the narrow outer shell of the particle, the scattering curves are similar. In Fig. 10 Porod's product as a function of hR is presented for L-A and Cos-A particles with $p = 0.9$, and compared with the homogeneous sphere to which Porod's law strictly applies. It will be seen that the maxima have nearly the same location and that the slope is slightly smaller for the Cos-C particle than for the L-A particle, but both scattering curves show a negative deviation from Porod's law. As shown by Ruland[4)], such a small deviation from Porod's law can be used to find the width of the transition layer if the electron density transition is limited to the narrow surface layer of one phase in the case of an irregular two-phase system (in which case no subsidiary maxima appear in the scattering curve).

5. *Conclusions*

Scattering curves for the following models of spherically symmetric particles of non-uniform electron density were calculated:

— model A, electron density decreases gradually from maximum value to the density of the surrounding medium, the transition being restricted to the outer shell of the particle;

— model B, the electron density transition is partly gradual and partly sharp. Three shapes of the gradual electron density transitions were studied: linear, cosine and Gaussian.

Some general features of the scattering curves, known for homogeneous particles, were also confirmed for inhomogeneous particles. They are the Gaussian course in the small angle region, known as Guinier approximation, and the dependence of the overall intensity of scattered radiation in the reciprocal space, known as invariant, on the average square of electron densities.

All scattering curves (one exception is the infinite particle which has the pure electron density distribution) oscillate at large angles round a curve which runs proportionally to h^{-n}, where h is proportional to the scattering angle. For all finite particles a simple asymptotic law could be found. The exponent n for the particles represented by model A is greater than 4 and depends on the type of electron density distribution. The width of the shell in which the electron density transition takes place, determines the angle from which the simple asymptotic law becomes valid.

Whenever the transition of electron density is partly sharp (model B), the value of n becomes 4. This result does not depend on which of the functions represents the electron density distribution, or on whether the abrupt drop of electron density is small or large, whether it is inside of the particle or at its edge, or on whether the central part of the particle is homogeneous or not. However, the angle at which the h^{-4} law is attained, depends on the special model considered. The constant product $h^4 I_{average}$ in this angular region is proportional both to the surface of a sphere at the edge of which the sharp transition of the electron density occurs and to the height of the electron density drop.

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CENTRALNO RASPRŠENJE RENDGENSKIH ZRAKA NA NEHOMOGENIM SFERNIM ČESTICAMA

K. KRANJC

Institut za fiziku Sveučilišta, Zagreb

Sadržaj

Izračunate su krivulje raspršenja rendgenskih zraka pod malim kutem za ove modele sferno simetričnih čestica:

— model A, elektronska gustoća kontinuirano pada u vanjskom sloju čestice do gustoće okolnog medija, i

— model B, prijelaz elektronske gustoće je djelomično kontinuiran a djelomično oštar.

Sve dobivene krivulje raspršenja imaju neka svojstva poznata za homogene čestice: oblik Gaussove krivulje, ovisne o polumjeru giracije, kod malih kuteva (Guinierova aproksimacija) i proporcionalnost ukupnog raspršenja u recipročnom prostoru sa srednjom vrijednosti kvadrata elektronske gustoće (invarijanta).

Za asimptotsko vladanje svih dobivenih krivulja raspršenja vrijedi jednostavan zakon da je prosječni intenzitet proporcionalan h^{-n} (h je proporcionalan kutu raspršenja). Eksponent n je za model A veći od 4: za linijski pad elektronske gustoće $n = 6$, a ako je raspodjela elektronske gustoće opisana cosinus funkcijom, $n = 8$. Postoji li skok u elektronskoj gustoći čestice, bio on malen ili velik, unutar čestice ili na njezinu rubu, eksponent $n = 4$, tj. ispunjen je Porodov zakon koji vrijedi i za homogene čestice. Konstantna vrijednost Porodovog produkta $h^4 \langle I \rangle$ proporcionalna je površini kugle na čijoj granici je skok, i dubini skoka, te o tome treba voditi računa kod uobičajenog korištenja Porodovog zakona za određivanje specifične površine.