# THEORY OF LIGHT SCATTERING BY SEMIRIGID MACROMOLECULES. THE STATISTICAL ZIGZAG MODEL

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## Abstract

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# THEORY OF LIGHT SCATTERING BY SEMIRIGID MACROMOLECULES. THE STATISTICAL ZIGZAG MODEL

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Up to the present time, regular zigzags, formed by rods of equal length, and the persistent chain with continuously distributed flexibility have been considered as the principal models of linear semirigid macromolecules. The persistent-chain model describes well the geometrical properties of macromolecules whose main mechanism of flexibility is associated with torsional oscillations of the links. If, however, the flexibility of the chain is caused by sharp disturbances of the short-range order (for example, in a rotational-isomeric mechanism), then neither the regular zigzag nor the persistent thread can serve as a suitable model. Indeed, in the persistent model kinks are not considered at all, while in the regular zigzag their statistical distribution along the chain, which apparently occurs in real macromolecules, is not taken into account. To describe such molecules, the statistical-zigzag model was proposed ([1]), in which the probability $p$ of a kink between neighboring links was introduced. If the chain is infinitely long, then the probability of the occurrence of a segment without kinks, consisting of $m$ links, is

$$f(m) = p(1-p)^{m-1}p, \tag{1}$$

the mean number of links in a rigid segment is

$$\langle m \rangle = \sum_{m=1}^{\infty} m f(m) \Big/ \sum_{m=1}^{\infty} f(m) = \frac{1}{p}. \tag{2}$$

and the fraction of rods consisting of $m$ links is

$$W(m) = f(m) \Big/ \sum_{m=1}^{\infty} f(m) = \frac{1}{\langle m \rangle} \left(1 - \frac{1}{\langle m \rangle}\right)^{m-1} \simeq \frac{1}{\langle m \rangle} e^{-\frac{m-1}{\langle m \rangle}} *. \tag{3}$$

If it is assumed that the distribution of the lengths of $n$ rigid segments in the macromolecule is independent (which, strictly speaking, is valid only for an infinitely long chain), then the probability of the occurrence of a chain consisting of a sequence of rods of lengths respectively $l_1, l_2, \ldots, l_n$ can be represented in the form

$$W(l_1, l_2, \ldots, l_n) = W(l_1)W(l_2) \ldots W(l_n) \simeq \left(\frac{l_0}{\langle l \rangle}\right)^n \exp\left(-\frac{l_1 + l_2 + \cdots + l_n}{\langle l \rangle}\right), \tag{4}$$

where $\langle l \rangle = \langle m \rangle l_0$ is the mean length of a rigid segment ($l_0$ is the length of one link).

Let us consider the indicatrix of scattering of light (and X-rays) by a freely jointed statistical zigzag. The scattering intensity for

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* It is not difficult to see that the exponential form of the expression is valid for $p \ll 1$ and $m/\langle m \rangle^2 \ll 1$.

of this model

$$I(\mu) = \langle I(\mu, l_1, l_2, \ldots, l_n) \rangle =$$

$$= \sum_n P_n \iint \cdots \int W(l_1, l_2, \ldots, l_n) I(\mu, l_1, l_2, \ldots, l_n)\, dl_1\, dl_2 \cdots dl_n, \tag{5}$$

where the probability of a configuration with $n$ bends, $P_n$, is described by a Poisson distribution. For $\langle n \rangle = N/\langle m \rangle \gg 1$ ($N$ is the number of links in the chain) this distribution is sufficiently narrow, and the sum in formula (5) may be replaced by one term with $n = \langle n \rangle$.

$$I(\mu, l_1, l_2, \ldots, l_{\langle n \rangle}) = \frac{2}{N^2} \left\{ \sum_{x=1}^{\langle n \rangle} \left[ l_x^2 \Lambda(\mu l_x) - \frac{2}{\mu^2} \sin^2\left(\frac{\mu l_x}{2}\right) \right] + \right.$$

$$\left. + \sum_{x=2}^{\langle n \rangle} \sum_{\rho=1}^{x-1} \Lambda(\mu l_x) \Lambda(\mu l_\rho)\, l_{x l_\rho} \sum_{k=\rho+1}^{x-1} \frac{\sin \mu l_k}{\mu l_k} \right\} \tag{6}$$

is the scattering intensity at an angle $2\theta$ by a zigzag with a given sequence of rod lengths (see (2)); $\mu = \frac{4\pi}{\lambda} \sin\theta$, $\lambda$ is the wavelength,

$$\Lambda(\mu l) = \frac{1}{\mu l} \operatorname{si}(\mu l)$$

(si($\mu l$) is the sine integral). Using approximation (4), we have:

$$I(\mu) = \frac{2}{N^2}\left(\frac{z}{1-z}\right)\left[\langle n\rangle - \frac{z^2}{1-z}\left(1 - z^{\langle n\rangle}\right)\right], \tag{7}$$

where $z = \text{arctg}\ \mu\langle l\rangle/\mu\langle l\rangle$. For small $\mu$, according to (7):

$$I(\mu) = 1 - \frac{\langle n\rangle\langle l\rangle^2}{9}\,\mu^2 + \ldots = 1 - \frac{L\langle l\rangle}{9}\,\mu^2 + \ldots, \tag{8}$$

where $L = \langle n\rangle\langle l\rangle$ is the contour length of the chain.

As is known, the coefficient of $\mu^2$ is $-\langle R^2\rangle/3$ ($\langle R^2\rangle$ is the mean square radius of gyration of the chain), whence

$$\langle R^2\rangle = L\langle l\rangle/3, \tag{9}$$

which is twice as large as for a regular zigzag with the same contour length and rod lengths $l = \langle l\rangle$.

On the other hand, it is not difficult to obtain an expression for the quantity $\langle R^2\rangle$ from geometrical considerations. From relations (1) and (2) it follows that, for the mean length $\langle l\rangle$ of a rigid segment,

$$\langle l^2\rangle = 2\langle l\rangle^2, \tag{10}$$

and, in the case of free jointing, the mean square distance between the $i$-th and $j$-th links is

$$\langle r_{ij}^2\rangle = \sum_k \langle l_k^2\rangle = \langle n_{ij}\rangle\langle l^2\rangle = 2\langle n_{ij}\rangle\langle l\rangle^2 = 2(j-i)l_0\langle l\rangle, \tag{11}$$

where $\langle n_{ij}\rangle$ is the mean number of bends between the given links. Starting from the definition of $\langle R^2\rangle$ and using (10), we obtain an expression completely coinciding with (9).*

Let us now consider the asymptotic behavior of formula (7). In works ([5,6]) it was shown that the relative scattering intensity by semiflexible chains at large values of $\mu$ has the form

$$I^{-1}(\mu) = A\mu + B, \tag{12}$$

where $A = L/\pi$, and for sufficiently long freely jointed regular zigzags with rod length $l$

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

$$B = -\frac{2L}{\pi^2 l}\left(\frac{\pi^2}{4} - 1\right). \quad (13)$$

* Expression (11) is valid, strictly speaking, for $(j-i) > \langle m \rangle$. But since, in calculating $\langle R^2 \rangle$, terms with large $(j-i)$ are especially significant, the use of the indicated formula for calculating all $\langle r_{ij}^2 \rangle$ apparently does not introduce a substantial error.

Since the quantity $B$, as follows from the analysis, is determined only by the number of bends, expression (13) also proves valid for a statistical zigzag, if $l$ is understood as $\langle l \rangle$. As is not difficult to show, for large $\mu$ formula (7) leads to the dependence (12), with $A$ and $B$ completely coinciding with the values indicated above.

Thus, the analysis carried out shows that expression (6) strictly describes the initial and asymptotic regions of the scattering curve of a statistical zigzag, which indicates the applicability of formula (7) over the entire range of scattering angles.

**Fig. 1.** The solid line corresponds to formula (7) with $\langle l \rangle = 64$ and $\langle n \rangle = 37.5$; the points are the calculation by machine at $p = 1/64$ and $N = 2400$ (averaging over 30 configurations)

**Fig. 2.** 1—scattering from a statistical zigzag with $\langle l \rangle = 7.5$ and $\langle n \rangle = 320$; 2—scattering from a regular zigzag with $a = l/2 = 7.5$ and $N = 2400$

Indeed, the approximation used concerning the independence of the lengths of the rigid segments in the chain is most significant at the very smallest scattering angles, when the X-rays "see" the dimensions of the individual rods, and least significant in the asymptotic region of scattering angles, in which the characteristic parameter is the mean number of bends, independent of the distribution of lengths of the rigid segments.

The considerations presented are fully confirmed by a numerical calculation, based on the Monte Carlo method, of the scattering indicatrix of a statistical zigzag with 2400 links and $p = 1/64$. To obtain the scattering curve: (a) a chain configuration was generated on a computer with a random distribution of rod lengths, determined by the probability of a bend $p$ after each link; (b) the function $I(\mu, l_1, l_2, \ldots, l_n)$ was computed from formula (6) for the given sequence of rods; and (c) the scattering intensity was averaged over all configurations obtained. As it turned out, after averaging $I(\mu, l_1, l_2, \dots, l_n)$ over 30–50 configurations, the fluctuations of $I(\mu)$ upon further increase of the count did not exceed a few percent.

Figure 1 gives the results of a computer calculation, represented by the dependence of $I$ on $\mu$, as well as the curve calculated from formula (7) with $\langle n \rangle = Np = 37.5$ and $\langle m \rangle = 1/p = 64$. As can be seen, the values $I(\mu)$ obtained on the computer (points) lie strictly on the theoretical curve over the entire range of scattering angles. It follows that expression (7), within the assumptions adopted ($p \ll 1,\ 1 \ll \langle n \rangle$), makes it possible to calculate with a high degree of accuracy the scattering curve for a freely jointed statistical zigzag.

Let us compare the behavior of the scattering intensity of regular and statistical zigzags in the dependence $I(\mu)\mu^2$ on $\mu$ (Fig. 2). As is known ([3,4]), in the indicated coordinates the small-angle X-ray scattering curve for a regular zigzag (as well as for a persistent chain) exhibits a bend whose abscissa $\mu_{\text{bend}}$ is related to the persistent length $a$ by the relation

$$\mu_{\text{bend}} a \sim 2. \tag{14}$$

At the same time, as is seen from Fig. 2, the scattering indicatrix for a freely jointed statistical zigzag is practically a straight line. This is due to the fact that, for a regular zigzag, there exists a wide range of values of $\mu$ in which the scattering from the individual rods may be considered constant ([7]), whereas for a statistical zigzag this region is shifted toward smaller $\mu$ owing to the polydisperse distribution of the rods with respect to length. Therefore, from the character of the scattering curve in the region under consideration, one can distinguish between a regular zigzag and a persistent chain, on the one hand, and a statistical zigzag, on the other. Since, as was already indicated above, the model of a regular zigzag is apparently not very realistic, the proposed method makes it possible to discriminate between the two most important models of linear macromolecules—the freely jointed statistical zigzag and the persistent chain.

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*Note: Figure translations are in progress. See original paper for figures.*