On the Interpretation of the Data Obtained by 3D Light Scattering Measurements

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Radiation-scattering experiments are a widely used tool to get some insight into the structure of matter. They have, therefore, frequently been applied to study the size of polymer molecules in dilute solutions. A quantity that, for example, can be determined by these methods is the structure factor, which is intimately correlated with the mean-square radius of gyration. Although it is well known by simulation results[1,2] that the instantaneous shape of a polymer chain is an ellipsoid rather than a sphere, this fact cannot be verified experimentally because of the isotropy of quiescent solutions. In this case no direction in space is favored, and the effects caused by the anisotropy of the coils are averaged out. The uniform distribution of the axes of the ellipsoids, however, is disturbed if a shear rate is applied. The orientation of the ellipsoidal coils becomes anisotropic, and in addition a coil deformation may take place.

The influence of these phenomena on the scattering behavior has already been described by several authors.[3-6] Springer and co-workers[6] developed an instrument that is able to measure the scattering intensity in several planes, thus extending the measuring features into the third dimension. This is in contrast to conventional instruments, where the detector can only be moved in one plane.

The theoretical foundations which all these authors used to analyze their scattering data are, however, somewhat ambiguous. The purpose of this paper is to present a procedure to interpret scattering data which is free from additional assumptions.

The starting point of the consideration is the well-known definition of the structure factor

$$S(k) = \frac{1}{N}\langle \sum_{m,n} e^{i\mathbf{k}\cdot\mathbf{r}_{mn}} \rangle \qquad (1)$$

where the symbols have the following meanings: N is the number of scattering centers with the positions $\mathbf{r}_j$ ($j \in \{1, 2, ..., N\}$), $\mathbf{r}_{mn} = \mathbf{r}_m - \mathbf{r}_n$, and $\mathbf{k} = \mathbf{k}_{in} - \mathbf{k}_{out}$ is the scattering vector defined as the difference between the wave propagation vectors for the incident and for the scattered beam; the angle between their directions is ϑ. Since photons scatter nearly elastically, $|\mathbf{k}_{in}| \approx |\mathbf{k}_{out}| = 2\pi/\lambda$, where λ is the wavelength of the radiation in the scattering medium. From these definitions follows $|\mathbf{k}| = k = (4\pi/\lambda)\sin(\vartheta/2)$. The summation is extended over all scattering centers.

For practical reasons a scattering function, $P(k)$, is frequently used, defined by

$$P(k) = \frac{S(k)}{S(0)} = \frac{1}{N^2}\langle \sum_{m,n} e^{i\mathbf{k}\cdot\mathbf{r}_{mn}} \rangle \qquad (2)$$

By series expansion of the exponential function one obtains

$$P(k) = 1 - \frac{1}{2N^2}\langle \sum_{m,n} (\mathbf{k}\cdot\mathbf{r}_{mn})^2 \rangle + ... \qquad (3)$$

The linear term of the expansion vanishes after performing the summation. Equation 3 can be written in a different way

$$P(k) = 1 - \mathbf{kk}{:}\frac{1}{2N^2}\langle \sum_{m,n} \mathbf{r}_{mn}\mathbf{r}_{mm} \rangle + ... \qquad (4)$$

$\mathbf{kk}$ is the dyadic product of the vectors $\mathbf{k}$. The term after the double dot is the radius of gyration tensor, $\mathbf{S}$.[1,7] This can easily be seen by a consideration similar to that leading to the theorem of Lagrange:[8] Let $\mathbf{s}_j$ be the vector from the center of gravity of the chain to the scattering center j, and $\mathbf{r}_G$ the position of the center of gravity. This means

$$\mathbf{r}_G = \frac{1}{N}\sum_j \mathbf{r}_j \quad \text{and} \quad \mathbf{s}_j = \mathbf{r}_j - \mathbf{r}_G$$

Starting from the definition of the radius of gyration tensor, one obtains

$$\begin{aligned}
\mathbf{S} &= \frac{1}{N}\langle \sum_j \mathbf{s}_j\mathbf{s}_j \rangle = \frac{1}{N}\langle \sum_j (\mathbf{r}_j - \mathbf{r}_G)(\mathbf{r}_j - \mathbf{r}_G) \rangle \\
&= \frac{1}{N}\left\langle \sum_j \left(\mathbf{r}_j\mathbf{r}_j - \frac{1}{N}\sum_i \mathbf{r}_i\mathbf{r}_j - \frac{1}{N}\sum_i \mathbf{r}_j\mathbf{r}_i + \frac{1}{N^2}\sum_{i,k} \mathbf{r}_i\mathbf{r}_k \right) \right\rangle \\
&= \frac{1}{N}\langle \sum_j \mathbf{r}_j\mathbf{r}_j \rangle - \frac{1}{N^2}\langle \sum_{i,j} \mathbf{r}_i\mathbf{r}_j \rangle \\
&= \frac{1}{2N^2}\langle \sum_{i,j} (\mathbf{r}_i - \mathbf{r}_j)(\mathbf{r}_i - \mathbf{r}_j) \rangle = \frac{1}{2N^2}\langle \sum_{i,j} \mathbf{r}_{ij}\mathbf{r}_{ij} \rangle
\end{aligned}$$

This gives in matrix notation

$$\mathbf{S} = \begin{pmatrix} S_{xx} & S_{xy} & S_{xz} \\ S_{xy} & S_{yy} & S_{yz} \\ S_{xz} & S_{yz} & S_{zz} \end{pmatrix}$$

with

$$S_{\alpha\beta} = \frac{1}{2N^2}\langle \sum_{m,n} r_{mn\alpha} r_{mn\beta} \rangle$$

and $\alpha,\beta \in \{x,y,z\}$. The trace of $\mathbf{S}$ is the mean-square radius of gyration. Thus

$$P(k) = 1 - k^2\mathbf{k}^0\mathbf{k}^0{:}\mathbf{S} + \mathcal{O}(k^4) \qquad (5)$$

$\mathbf{k}^0$ is the unit vector pointing in the direction of $\mathbf{k}$. $\mathbf{k}^0\mathbf{k}^0{:}\mathbf{S}$ is a quadratic form in the coordinates of $\mathbf{k}^0 = (k_x, k_y, k_z)^T$ as variables and in the $S_{\alpha\beta}$ as coefficients. As can be seen from eq 5, this form can be determined as the slope of the plot $P(k)$ versus k^2 at $k = 0$. To obtain a connection between the mathematical formalism and the geometry of the 3D-scattering instrument described by Link and Springer,[6] an illustration is used which is similar to Figure 2 of the paper cited (Figure 1). The diagram is provided with a (left-handed) coordinate system with its origin in the scattering cell. The z-axis points in the direction of the incident beam and the x-axis in the flow direction. In this system the wave propagation vectors can be described by $\mathbf{k}_{in} = (2\pi/\lambda)(0, 0, 1)^T$ and $\mathbf{k}_{out} = (2\pi/\lambda)(\sin\vartheta\cos\varphi, \sin\vartheta\sin\varphi, \cos\vartheta)^T$. ϑ and φ are spherical coordinates.

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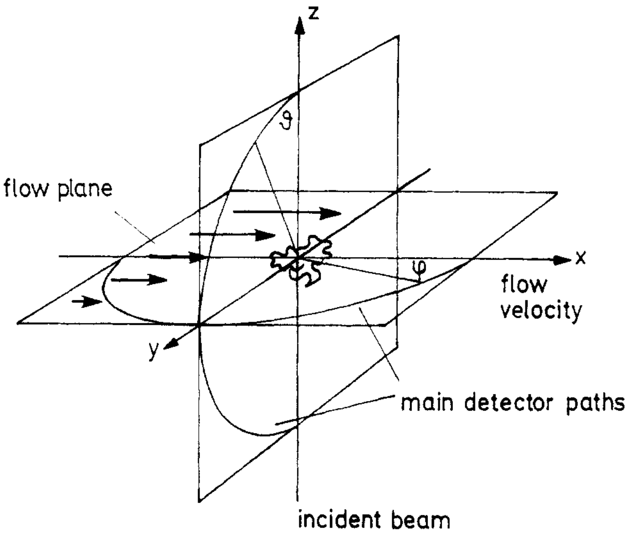

Figure 1. Schematic diagram of an instrument to measure the radiation scattering of a polymer solution under shear stress.[6]

They characterize the position at which the scattering intensity is measured. From this follows

$$\mathbf{k} = \frac{2\pi}{\lambda}\begin{pmatrix} -\sin\vartheta\cos\varphi \\ -\sin\vartheta\sin\varphi \\ 1-\cos\vartheta \end{pmatrix} = \frac{4\pi}{\lambda}\sin\frac{\vartheta}{2}\begin{pmatrix} -\cos\frac{\vartheta}{2}\cos\varphi \\ -\cos\frac{\vartheta}{2}\sin\varphi \\ \sin\frac{\vartheta}{2} \end{pmatrix} = k\mathbf{k}^0$$

Therefore

$$\mathbf{k}^0\mathbf{k}^0{:}S = S_{xx}\cos^2\frac{\vartheta}{2}\cos^2\varphi + S_{yy}\cos^2\frac{\vartheta}{2}\sin^2\varphi + S_{zz}\sin^2\frac{\vartheta}{2} + S_{xy}\cos^2\frac{\vartheta}{2}\sin 2\varphi - S_{xz}\sin\vartheta\cos\varphi - S_{yz}\sin\vartheta\sin\varphi \quad (6)$$

The six unknowns $S_{\alpha\beta}$ can be calculated by setting up a system of (at least) six equations. For this purpose measurements with different wavelengths have to be performed at a fixed position of the detector to determine $f(\vartheta,\varphi)$ (see eq 5). This procedure has to be repeated at least five times with other detector positions. The simultaneous linear equations can easily be solved by one of the usual numerical methods, or—if applicable—by the methods of linear multiple regression. The radius of gyration tensor can now be diagonalized by a similarity transformation

$$\mathbf{S} = \mathbf{Q}\cdot\mathbf{L}\cdot\mathbf{Q}^{-1}$$

The spectrum of **S** represented by the diagonal elements of **L** is identical with the set of the principal components of the mean-square radius of gyration, whereas the column vectors comprising **Q** contain the components of the respective principal axes expressed in the reference basis system.

References and Notes

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