Stochastic Order in Macromolecular Solutions: a SANS Experiment

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A SANS experiment has been performed in solutions of ß-lactoglobulin at different concentrations. According to previous results, a definite structure factor can be extracted, besides a careful evaluation of the form factor. The results are discussed within the frame of a phenomenological stochastic model that allows parametrization of the experimental results in terms of preferred lengths. The occurrence of preferred lengths, almost independent from the concentration, suggests the existence of well defined local structures in which both spatial and rotational orders are involved. A suggestion from the numerical values of the implied parameters points to a distance of 120 Å that would characterize the interaction potential.

1. GENERAL SURVEY

The results presented in the present paper are part of the investigation pursued by our group in the last years. This investigation concerns the anomalous properties exhibited by macromolecular solutions. Therefore, it seems useful to sketch briefly the results obtained to date using different experimental techniques1 together with a phenomenological model that allows a unitary description of the observed phenomena.

Macromolecules in aqueous solutions are very complicated systems, because of their, up to now not fully understood, interaction potential, which is due mainly to the surface charge distribution, as well as to the ionic properties of the solvent.
Various models have been proposed, the most general being probably the so called DLVO potential. A dynamical origin was also proposed for the interaction via a dipole–dipole resonance, which can give rise either to an attractive or to a repulsive contribution, depending on the dielectric properties of the medium. A common feature of the proposed models is the presence of a secondary minimum, which would be influenced by the structural properties of the macromolecular solutions.

We studied rheological properties, static and dynamic light scattering, acoustic and hypersonic measurements and elastic and inelastic neutron scattering.

All the obtained results indicate that macromolecular solutions cannot be considered to be homogeneous systems, even on a semi-macroscopic scale. Physical properties fluctuate with correlation lengths up to thousands of Å, originating a hierarchy of 'structures' that are reflected also in dynamic behaviour. The systems show thixotropic properties as well as a non-locality in diffusion processes. Also, the diffusional behaviour of the solvent seems to be influenced by the structured distribution of macromolecules.

In order to obtain a unified description of the various observed phenomena, we developed a phenomenological stochastic model, having the advantage of being analytically solvable. This model allows parametrization of the obtained results without any explicit reference to a specific interaction potential. We simply assume that the system can be characterized by a characteristic length, which plays the role of a 'preferred distance', in terms of an equilibrium position determined by the nearest neighbours positions. The 'objects' of the model can be single macromolecules or even fluctuating semi-macroscopic volumes, so that it can be applied to describe a microscopic behaviour (e.g. in a neutron scattering-experiment) as well as large scale fluctuation patterns (e.g. in a light scattering experiment).

In this model, a point scatterer obeys a Langevin-like dynamical equation, around an instantaneous equilibrium position, described by the characteristic length. According to the ratio between the typical relaxation time and the mean–collision time, the point will behave either like a damped oscillator resembling a solid-like system, or like a brownian ensemble of diffusing particles.

Concerning the structural aspect of the model, it is possible to derive the following equation for the structure factor:

$$S(k) = 2 \frac{1 - \exp(-k^2\sigma^2/4) \cos(kL)}{1 - 2\sigma^2 k^2/4 \cos(kL) + e^{-k^2\sigma^2/2}}$$

(1)

where $k$ is the exchanged wave vector, $L$ the 'preferred distance' and $\sigma$ the rms of the stochastic displacements. Obviously, to describe the actual scattering experiment, the structure factor has to be multiplied by a suitable 'form factor', which depends on the shape of individual scatterers.

As mentioned above, eq. (1) allows parametrization of the results obtained in a scattering experiment in terms of the two parameters, $L$ and $\sigma$. This procedure has been successfully applied in a SANS experiment performed on a lysozyme solution.

The relevant result consists of the evaluation of a preferred distance $L$, systematically smaller than the mean distance between macromolecules $\bar{d}$ evaluated according to the number concentration: $\bar{d} = n^{-1/3}$, suggesting the existence of regions of higher concentrations. In addition, $L$ is scarcely affected by the concentration, as one would
expect, if \( L \) enters as a characteristic parameter in an unknown interaction potential, which cannot be a purely repulsive one. Obviously, there is a "critical" concentration at which \( L = \bar{d} \) at this concentration (that for the lysozyme solutions turns out to be about 20% by weight), regions characterized by a mean distance \( L \) are no longer distinguishable from the remaining part of the system. This conclusion is experimentally supported both by the light scattering experiment and by the disappearance of the thixotropic properties of the system at the critical concentration.

In the present paper we report the results obtained in a SANS experiment in solutions of \( \beta \)-lactoglobulin. In comparison with the experiment of ref. 10, we cover a wider range of exchanged wavevectors and, in addition, a better statistic is obtained. As a consequence, a more careful analysis of the data can be performed. We will see that although eq. (1) can fit the data with reasonable accuracy, a significant improvement is possible if more that one preferred distance is allowed in an improved version of our stochastic model. This approach is discussed in sec. 3, while in sec. 4 we apply the formalism to our experimental spectra. The obtained results allow a deeper insight into the structural behaviour of this kind of systems, indicating the possibility of a quasi-crystalline local structure at the origin of the observed properties.

2. MATERIALS AND DATA HANDLING

\( \beta \)-lactoglobulin is a globular protein with a molecular weight of 34,000 daltons, formed by two subunits of 17,000 daltons each \( \beta \)-lactoglobulin and D₂O (98% pure) were purchased from Sigma Chem. Co. The protein was further dialyzed for three days against distilled and deionized water using Spectra Por/7 membrane and then it was freeze-dried. All the measurements were performed at constant room temperature. The investigated samples were solutions of the protein in D₂O at different concentration by weight, namely 5%, 15%, 20% w/w. The measured pH value is 7.6 while the isoelectric point is 5.2. Another measurement at 2% by weight was performed at high ionic strength using a 0.07 M NaCl solution. We studied these systems by means of small angle neutron scattering. In this technique, due to the low spatial resolution (5–10 Å), the scattering intensity at a given wavevector \( k = (4\pi/\lambda)\sin(\theta/2) \) can be written as

\[
I(k) = A F(k) S(k)
\]  (2)

\( F(k) \) being the form factor of the macromolecule and \( S(k) \) the inter-proteins structure factor and \( A \) takes into account the proteins concentrations and the scattering efficiency. Equation (1) splits the scattered intensity into a contribution coming from the protein itself, depending on its shape and size, and another contribution coming from the spatial distribution of the proteins.

The instrument used for the experiments was the PAXE small angle spectrometer at the ORPHEE reactor (CEA-CEN Saclay). The spectra were taken for each sample using two different spectrometer configurations (changing the incident wavelength and the sample to detector distance). In this way, we were able to cover two partially overlapping \( k \)-ranges: 0.01–0.1 Å⁻¹ and 0.05–0.36 Å⁻¹.

The data were collected by means of a two-dimensional detector, converted in intensity versus \( k \) and normalized for transmission and sample path length. Then, in order to obtain an absolute intensity scale, the data were normalized to a water run.
It is worth noticing that normalized spectra belonging to different $k$-ranges, partially overlapping, match very well. The experimental results are shown in Figure 1.

Concerning the form factor, the shape of a globular protein is well represented by an ellipsoid with semiaxes $a$, $b$ and $c$ and volume $V = 4\pi abc/3$. The scattered intensity by a prolate ellipsoid ($b=c$) is given by \(^{11,12}\)

$$F(k) = \int_0^1 \left( \frac{3J_1(u)}{u} \right) du$$

with

$$u(\mu) = k\sqrt{a^2\mu^2 + b^2(1 - \mu^2)}$$

and

$$J_1(x) = \frac{\sin(x) - x\cos(x)}{x^2}$$

Fits of experimental data using eq. (2) provide the best values for the semiaxes of the ellipsoid that better represents the protein under investigation. The fit procedure can be made easier by knowing the protein volume in solution. This information can be obtained, with good accuracy, using different techniques.\(^{13,14}\)

From the experimental point of view, we carried out measurements on a sample obtained by dissolving the 0.02 w/w of $\beta$-lactoglobulin in a 0.07 M NaCl solution. The low concentration and the high ionic strength (whose purpose is to screen the charged polar groups of the protein) make all structural contributions in the scattered intensity practically negligible. Figure 2 shows the fit of the experimental data. The fit proce-
Figure 2. β-lactoglobulin solution 0.02 w/w in D₂O and 0.07 M NaCl. Fitted form factor.

Figure 3. (a) Amplitude of the scattered intensity, (b) Background of experimental spectra, (c) S(O) values.

dure provides the values for $A$, $a$, and an additive background $f$, $b$ can be calculated using $a$ and the known volume of the protein. The obtained values for the semiaxes are: 58.8 Å and 14.3 Å.

This result is in good agreement with the literature results. Once that the shape of the protein is known, the structure factor can be obtained, provided that the values
for \( A \) can be determined for the higher concentration solutions. This can be obtained by fitting the high concentration data, with eq. 2, in a \( k \)-range \((\geq 0.3 \text{ Å}^{-1})\) where \( S(k) \) is assumed to be very close to unity. The obtained values for \( A \) and \( f \) are shown in Figure 3 as a function of the protein concentration. Both of them grow linearly with concentration, as one can expect. In particular, the intercept of \( f \) well agrees with the expected scattering intensity from pure water. Figure 3 also shows the osmotic compressibility \( \chi - S(0) \), which decreases with concentration.

The obtained results for the \( S(k) \) will be discussed in section 4.

3. THE IMPROVED STOCHASTIC MODEL

The structure factor \( S(k) \) for a system of \( N \) scattering points at positions \( R_i \) is given by

\[
S(k) = \sum_{i,j} \exp[ik(z_i - z_j)] - 1
\]

(4)

where \( z_i \) is the coordinate of \( \mathbf{R}_i \) along the \( z \)-axis, parallel to the exchanged wavevector \( k \). In our model, the nearest neighbours distance is given by

\[
R_{i+1} - R_i = L + \varepsilon_i
\]

where \( L \) is the 'preferred' distance, while \( \varepsilon_i \) is a time dependent stochastic variable obeying a Langevin-like equation. Here, we are interested in the stationary situation, \textit{i.e.} in the asymptotic value of \( \varepsilon_i \), which turns out to be a stochastic variable distributed according to a Gaussian law, with a rms \( \sigma \), whose value depends on some characteristic time.\(^6\) Therefore,

\[
(R_i - r_j) = nL + \sum_{s=0}^{N} \varepsilon_s
\]

(5)

with \( n = |j - i| \). Now, the sum in eq. (5) gives rise to a stochastic variable with rms \( \sigma = \sigma \sqrt{n} \). Therefore, performing a thermodynamic average on eq. (2) one obtains

\[
S(k) = 2\Re \sum_{n=1}^{N} \exp(iknL) \exp \left( -\frac{k^2 \sigma^2}{4} n \right) - 1
\]

(6)

where \( \Re \) indicate the real part. The presence of the negative real exponent allows the sum to be treated as an absolutely convergent geometrical series, so that eq. (1) easily follows.

Now, let us suppose that \( L \) can be either \( L_1 \) or \( L_2 \), and, correspondingly, \( \sigma \) can be either \( \sigma_1 \) or \( \sigma_2 \), according to the probabilities \( p \) and \( q = 1 - p \). We can treat the difference between \( L_1 \) and \( L_2 \) as an additional stochastic noise, by putting

\[
L_1 = L + \Delta L \quad \text{and} \quad L_2 = L - \Delta L
\]
where \( L = (L_1 + L_2)/2 \) and \( \Delta L = (L_1 - L_2)/2 \). Then, at the place of the quantity
\[
\exp \left( - \frac{k^2 \sigma_1^2}{4} n \right)
\]
in eq. (1), we have the mean value:
\[
\langle f(r) \rangle = \left\langle e^{i k (2r - n) \Delta L} \exp \left( - \frac{k^2 \sigma_1^2}{4} r \right) \exp \left( - \frac{k^2 \sigma_2^2}{4} (n - r) \right) \right\rangle
\]
where \( 0 \leq r \leq n \), \( r \) being the number of \( L_1 \) in a \( n \)-sample sequence, that is a stochastic variable obeying a Bernoulli binomial distribution, characterized by the probabilities \( p \) and \( q \). Therefore,
\[
\langle f(r) \rangle = \sum_{r=0}^{n} \exp \left( i k \Delta L - \frac{k^2 \sigma_1^2}{4} \right) \exp \left[ - \left( i k \Delta L - \frac{k^2 \sigma_1^2}{4} \right) (n - r) \right] \binom{r}{n} p^r q^{n-r} =
\]
\[
= \left[ p \exp \left( i k \Delta L - \frac{k^2 \sigma_1^2}{4} \right) + q \exp \left( i k \Delta L - \frac{k^2 \sigma_2^2}{4} \right) \right]^n
\]
We are again concerned with an absolutely convergent geometrical series, which now furnishes the following expression for the structure factor:
\[
S(k) = 2 \frac{1 - a}{1 - 2a + b} - 1
\]
where
\[
a = p \exp \left( - \frac{k^2 \sigma_1^2}{4} \right) \cos(kL_1) + q \exp \left( - \frac{k^2 \sigma_2^2}{4} \right) \cos(kL_2)
\]
\[
b = p^2 \exp \left( - \frac{k^2 \sigma_1^2}{4} \right) \cos(kL_1) + q^2 \exp \left( - \frac{k^2 \sigma_2^2}{4} \right) \cos(kL_2) +
\]
\[
+ 2pq \exp \left( - \frac{k^2 (\sigma_1^2 + \sigma_2^2)}{4} \right) \cos[k(L_1 - L_2)]
\]

Obviously, eq. (7) reduces to eq. (1) in the two limiting cases, \( p = 1 \) or \( p = 0 \). However, putting \( L_1 = L_2 \), eq. (7) does not reduce to eq. (1) unless \( \sigma_1 \) is equal to \( \sigma_2 \) as well. It is worthwhile noticing that eq. (7) is different from a simple superposition with weights \( p \) and \( q \) of two eqs. (1) because of the interference effects between the characteristic lengths.

From the physical point of view, our model describes an ensemble of particles for which the mutual distance between any couple of them can be separated in a regular part (\( nL \) or \( n_1L_1 + n_2L_2 \) with \( n_1 \) and \( n_2 \) integers) plus a stochastical contribution, which becomes more and more broadened at increasing distances (i.e. high values of \( n_1 \)). The very physical meaning of \( L \) comes only from such a construction, as an 'approximate greatest common factor' for all the actual values of mutual distances. Obviously, such a procedure could be also applied to any kind of actual distribution of molecules. For example, one can choose \( L = \bar{d} \), \( \bar{d} \) being the mean distance calculated according to the
number concentration $\bar{d} = \rho^{-1/3}$. In this case, the distance between any couple of molecules becomes $n\bar{d} + \varepsilon$, where $\varepsilon$ behaves as a random variable that will be distributed according to some distribution function $f(\varepsilon)$. It is clear that the kind of distribution function depends on the value arbitrarily chosen for $L$. Our model states that there is a choice (which can be different from $\bar{d}$) for which the distribution function becomes narrower, i.e. our preferred distance $L$ is the 'approximate greatest common factor' that minimizes the width of the distribution of differences between actual distances and integer multiples of $L$. In comparison, any other choice for $L$ will give rise to a distribution so broad that the choice itself for the value of the integer becomes questionable. As a consequence, in a scattering experiment, we expect the presence of more or less broadened peaks centered at wavevectors multiples of $2\pi/L$. In contrast, if our model allows a good fit with an experimental $S(k)$, the structural properties of the system under investigation can be described in the simplest way by such a model, and characterized by the two parameters $L$ and $\sigma$. Generalization to the case of two characteristic lengths is quite straightforward.

It could be pointed out that, assuming a sufficient number of different preferred lengths, any experimental result can be fitted. This is actually true. However, unless some definite physical meaning can be assigned to the different values of $L$, the use of the model will rapidly reduce to a kind of series expansion of the experimental data that simply transform $S(k)$ in the correlation function $g(r)$.

4. EXPERIMENTAL RESULTS AND DISCUSSION

In the model described in the previous section, we made the hypothesis that a selected component of the vectors $R_n$ namely the one parallel to the exchanged wavevector, behaves like an ill ordered stochastic variable. The 'density' of the coordinate $z_i$ along the $z$-axis corresponds to a 'planar density'

$$\hat{\rho}(z) \, dz = \int f(\vec{r}) \, d\vec{r}$$

where the integral is performed in the space limited by two planes orthogonal to the $z$-axis and spaced by $dz$. All the scatterers inside this slice give rise to coherently scattered wavelets, the phase changing only by moving along the $z$-axis. However, the assumption of isotropy, which characterizes a fluid, leads to

$$f(\vec{r}) = \frac{g(r)}{4\pi r^2}$$

where $g(r)$ is the density of probability of finding a molecule at a distance $r$ from the origin. In this case, $\hat{\rho}(z)$, according to eq. (8), turns out to be a function of $z$, in which the features of the radial distribution function $g(r)$ are partially smeared out. As a consequence, the structure factor $S(k)$, i.e. the Fourier transform of the autocorrelation function of $\hat{\rho}(z)$, can hardly show any feature that could be interpreted as a 'preferred distance'. In other words, if $f(\vec{r})$ is isotropic at all lengths scales, a scattering experiment will give a result quite insensitive to the behaviour of the radial correlation function, the information being concealed only in the derivative of the experimental $S(k)$. In such a way, the correctness of some assumed isotropic pair potentials can hardly be
checked from the experimental data. However, if there is a structural arrangement, able to give a 'preferred distance' also in the projection \( \rho(z) \), then such a distance can be easily extracted from the experimental \( S(k) \). The only way that could yield this result is the assumption that, at least for distances larger than, say, two or three times the 'preferred distance', the system can be considered neither homogeneous nor an isotropic one. Obviously, this local order cannot be obtained in a simple way starting from an isotropic pair potential, since it implies a collective behaviour of the system. In other words, if an experimental \( S(k) \) shows features that can be described in terms of one or more preferred distances, we are forced to assume a locally non-isotropic structure, like that of an ill ordered polycrystal. In addition, the founded preferred distances will refer to distances between planes, not between single particles. This situation was well known from the beginning of scattering techniques,\(^{11}\) although often not explicitly acknowledged. The advantage of our stochastic model is the possibility of parametrization of the experimental spectra, without any explicit reference to the interaction potential, the structural properties of the system being synthesized through the values of \( L \) and \( \sigma \), the latter taking also into account the orientational disorder.

In the last few years, attention has been focussed on some almost regular structures, called 'quasicrystal',\(^{15}\) in which the orientational order, in addition to the translational order, is considered. A peculiarity of these structures is that their diffraction pattern corresponds to the Fourier transform of a one-dimensional quasicrystal.\(^{19}\) This pattern shows peaks whose positions scale according to regular sequences generated by the 'golden mean' \( (1 + \sqrt{5})/2 \) (e.g. the Fibonacci sequence).

Consequently, our one-dimensional stochastic model seems appropriate for the empirical description of this kind of diffraction patterns. The most investigated structure is the icosahedral one. Icosahedrons cannot fill the space, which gives rise to a 'frustration' leading to a long range increasing disorder. This structure, however, turns out to be the closest to spherical symmetry, even closer than the close-packed fcc structure. As far as our experimental results are concerned, we found that a very good agreement can be obtained by fitting the experimental structure factor with

\[
S(k) = (1 - A)a(k) + Ab(k)
\]

(10)

where \( a(k) \) corresponds to eq. (1) (with \( L_3 \) and \( \sigma_3 \) as parameters), while \( b(k) \) refers to eq. (7) (with \( p, L_1, \sigma_1, L_2 \) and \( \sigma_2 \) as parameters). Figures 4, 5, 6 show the results of the fits, while the obtained values for the implied parameters are listed in Table I.

**TABLE I**

Results from the fitting procedure, (lengths are in angstrom)

<table>
<thead>
<tr>
<th>Conc. by weight</th>
<th>( A )</th>
<th>( L_3 )</th>
<th>( \sigma_3 )</th>
<th>( p )</th>
<th>( L_1 )</th>
<th>( \sigma_1 )</th>
<th>( L_2 )</th>
<th>( \sigma_2 )</th>
<th>( \bar{d} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.13</td>
<td>110</td>
<td>100</td>
<td>0.98</td>
<td>100</td>
<td>28</td>
<td>32</td>
<td>10</td>
<td>105</td>
</tr>
<tr>
<td>0.15</td>
<td>0.60</td>
<td>68</td>
<td>48</td>
<td>0.90</td>
<td>100</td>
<td>96</td>
<td>33</td>
<td>9</td>
<td>72</td>
</tr>
<tr>
<td>0.20</td>
<td>0.60</td>
<td>57</td>
<td>30</td>
<td>0.60</td>
<td>81</td>
<td>37</td>
<td>32</td>
<td>16</td>
<td>65</td>
</tr>
</tbody>
</table>

Here \( \bar{d} \) is the 'mean distance' calculated according to the number concentration \( \bar{d} = \rho^{-1/3} \).
Let us now discuss briefly the obtained results. First of all, we recall that $L$ cannot be general considered a nearest neighbour distance, since it refers to the distance between planes, measured along the direction of the exchanged wavevector. Table 1 shows the existence of two preferred distances, $L_1$ and $L_2$, which seem quite insensitive to the concentration (at least up to a 15% concentration by weight as far as $L_1$ is concerned). In contrast, the third distance $L_3$ roughly scales like $\overline{d}$. As mentioned above,
Figure 6. $\beta$-lactoglobulin solution 0.20 w/w in D$_2$O. Fit of the structure factor. (a) from eq. (1), (b) from eq. (7), (full line) total fit.

The use of eq. (4) does not correspond to a simple superposition of two eq. (1), because of the interference between $L_1$ and $L_2$. The fact that the best fit is obtained by attributing $L_1$ and $L_2$ to eq. (4) and $L_3$ to eq. (1) (the agreement is much worse for other choices) suggests that both $L_1$ and $L_2$ are to be related to some structural arrangement that takes place beside the trivial one described by $L_3 = \rho^{-1/3}$. This conclusion is also supported by the comparatively smaller values of the rms $\sigma_1$ and $\sigma_2$.

In this case, parameter $A$ roughly measures the amount of the ordering tendency. It can be noticed that this tendency is also evidenced by the need of two entirely different values for $\sigma$ for nearly the same distance, at a 5% by weight concentration, when besides $L_3$ also $L_1$ approaches $d$.

It is, therefore, reasonable that $A$ increases at increasing concentration up to a maximum value, above which the 'structure' becomes more and more distorted.

The presence of some preferred distances seems unquestionable, even from a crude examination of the experimental spectra, our fitting having solely the meaning of a useful parametrization. As mentioned above, experimental results of this kind would imply that orientational order must, to some extent exist, in the system. Of course, any kind of structures, as well as any kind of interaction potentials, able to give rise to the desired distances among pseudo-crystallography planes, could be compatible with our experimental results, because there is not a unique way to pass from a measured $S(k)$ to a defined $f(\tau)$. If, tentatively, we think of an icosahedral structure, our results can be compared with a theoretical calculation that furnishes the position of the peaks in the diffraction pattern, in terms of a quasilattice constant.$^{17}$ Actually, our values of $L_1$ and $L_2$ correspond to two of the more intense peaks calculated in ref. [17], provided that a quasilattice constant of 120 Å is assumed. It can be noticed that also assuming an fcc structure, the distance between the 111 planes turns out to be very close to $L_1$, if the tetrahedron edge is put equal to 120 Å.
5. CONCLUDING REMARKS

The results obtained in the present experiment fit very well the general picture of the behaviour of macromolecular solutions. Apart from the work of our group, there are a large number of experimental results that show the existence of a more or less pronounced structure factor, which in turn calls for some suitable interaction potential.\textsuperscript{18,20}

In other words, macromolecular solutions are far from being homogeneous systems. In contrast, a well defined correlation must exist among the macromolecular positions. SANS experiments are able to reveal such a correlation. Like in the case of lysozyme,\textsuperscript{10} also in the $\beta$-lactoglobulin solutions the structure factor reveals the existence of some 'preferred distance', showing up above a stochastic noise.

The model equations that we use in order to fit the data do not add anything, being free from any physical assumption. In fact, besides the specific mathematical procedure from which eqs. (1) and (4) can be derived, the only assumption concerns the possibility of parametrization of the 'projected' planar density $\rho(z)$ in terms of one or more preferred distances. The correspondence between such a possibility and a successful fit of the experimental data with our model is biunivocal.

On the other hand, as mentioned above, the one-dimensional $\hat{\rho}(z)$ can possess features describable in terms of preferred distances if, and only if, the tridimensional molecular arrangement $f(r)$ possesses not only a radial, but also an angular correlation.

If, in addition, one takes into account that the very size of the molecules is not negligible, compared to the distances implied in the structure, the latter must be very peculiar, involving not only the centre-of-mass position but also the orientation of the molecules.

As an example, a local structure of the kind of an fcc crystal having a side length of 100 Å cannot be observed if the molecules, whose length is ~100 Å, are aligned along the 111 direction. In this case, the local order is not reflected in the $\rho(z)$. Notwithstanding, our experimental results (among many others) clearly indicate that some sort of structure must exist.

The careful evaluation of the preferred distances in the present experiment allows one to consider a possible candidate for the kind of structure involved. There are orientationally invariant structures that are not invariant under translation: the so-called quasicrystals. Some of them possess a high degree of spherical symmetry (in a local frame of reference), which is a fundamental property of liquid phases. The most promising structure could be an icosahedral one. If this is the case, the fundamental property of the interaction potential must be the allowance for a preferred distance of 120 Å.
REFERENCES


SAŽETAK

Stohastički red u makromolekularnim otopinama: eksperiment raspršenja neutrona pod malim kutom (SANS)

**R. Giordano, A. Grasso, J. Teixeira, F. Wanderlingh i U. Wanderlingh**

SANS eksperiment proveden je u otopinama β-laktoglobulina različitih koncentracija. U skladu s prijašnjim rezultatima može se osim pažljive evaluacije faktora oblika izvesti i odredjen strukturni faktor.

Rezultati su prodiskutirani u okviru fenomenološkoga stohastičkog modela koji dopušta parametrizaciju eksperimentalnih rezultata s pomoću preferiranih duljina. Pojavljivanje preferiranih duljina, gotovo neovisno o koncentracijama, navodi na zaključak o postojanju dobro definiranih lokalnih struktura sa spacijalnom rotacijskom uređenostu. Predloženo je da bi se s pomoću numeričkih vrijednosti uključenih parametara te indiciranih distancija od 120 Å mogao karakterizirati potencijal interakcije.