The Inclination Angle of Nonisotropic Inhomogeneities Determined by SANS

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Abstract
The angle between the axis of symmetry of nonisotropic inhomogeneities and the surface of a bulk sample is sometimes unknown. This angle may be determined by fitting small-angle neutron scattering (SANS) data taken at two or more different sample inclination angles. The feasibility of this technique is verified by analyzing SANS data taken at different tilt angles from a well characterized hot-stretched (partially deuterated) polystyrene sample.

I. Introduction
Nonisotropic inhomogeneities in bulk materials are sometimes axially symmetric. The angle between the symmetry axis (when there is one) and the scattering plane can be extracted by making two or more small-angle neutron scattering (SANS) measurements at different sample inclinations. The focus of this paper is on the orientation of perdeuterated polystyrene chains (diluted in hydrogenated polystyrene) in a hot-stretched sample. After slight modification, this technique can be applied to other anisotropic systems (e.g. shale rocks with nonisotropic inhomogeneities such as micropores under uniaxial pressures).

Elliptical averaging is an efficient way of analyzing asymmetric SANS data (Mildner, 1983; Summerfield & Mildner, 1983). This technique was introduced by Reynolds & Mildner (1984) as an alternative to using two orthogonal slices (in the directions perpendicular and parallel to the symmetry axis) of the two-dimensional data and has been applied to anisotropic systems (e.g. shale rocks with nonisotropic inhomogeneities such as micropores under uniaxial pressures).

II. Scattering structure factor for uniaxially oriented polymer chains
Nonoriented polymer chains in the bulk follow Gaussian statistics. In order to derive the static scattering function $S(Q)$ for stretched (oriented) chains, these are also assumed to follow Gaussian statistics (ideal chains) in the directions parallel and perpendicular to the stretch axis. $S(Q)$ is given by

$$S(Q) = \left(\frac{1}{N^2}\right) \sum_{i=1}^{N} \sum_{j=1}^{N} \exp(iQ \cdot r_{ij})$$

$$= \left(\frac{1}{N^2}\right) \sum_{i=1}^{N} \sum_{j=1}^{N} \exp(-Q_x^2 \langle r_{ijx}^2/2 \rangle)$$

$$\times \exp(-Q_y^2 \langle r_{ijy}^2/2 \rangle)$$

$$\times \exp(-Q_z^2 \langle r_{ijz}^2/2 \rangle)$$

(1)

where $\langle \ldots \rangle$ is an average over equilibrium Gaussian distributions, $N$ is the number of scattering units (monomers) in a labeled polymer chain, $r_{ij}$ is the vector interdistance between monomers $i$ and $j$ and the three coordinates ($x, y, z$) are assumed to be uncorrelated. Moreover, chain portions are assumed to deform uniformly, i.e.

$$\langle r_{ijx}^2 \rangle = \langle r_{ijy}^2 \rangle$$

$$\langle r_{ijy}^2 \rangle = \langle r_{ijz}^2 \rangle$$

$$\langle r_{ijz}^2 \rangle = \langle r_{ij}^2 \rangle$$

(2)

with $e_x, e_y$ and $e_z$ independent of $i$ and $j$ and

$$\langle r_{ij}^2 \rangle = b^2 \langle |i-j| \rangle = \langle b^2 \rangle R_g^2 \langle |i-j| \rangle.$$

(3)

$R_g$ and $b$ are the radius of gyration of the labeled chain and its statistical unit length. With the following identity (valid for large $N$)

$$\left(\frac{1}{N^2}\right) \sum_{i=1}^{N} \sum_{j=1}^{N} F(|i-j|) = \left(\frac{2}{N}\right) \sum_{i=1}^{N} \left(1 - i/N\right) F(i),$$

(4)

$S(Q)$ can be put in the form

$$S(Q) = \left(\frac{2}{N}\right) \sum_{i=1}^{N} \left(1 - i/N\right)$$

$$\times \exp[-(Q_x^2 e_x^2 + Q_y^2 e_y^2 + Q_z^2 e_z^2)b^2 i/2]$$

(5)
which, going to the continuous limit, yields the usual Debye function

$$S(Q) = (2/X^2)[\exp(-X) - 1 + X]$$  \hspace{1cm} (6)

with a modified argument

$$X = (Q_x^2 a_x^2 + Q_y^2 a_y^2 + Q_z^2 a_z^2)Nb^2/2$$
$$= 3(Q_{x'}^2 R_{x'}^2 + Q_{y'}^2 R_{y'}^2 + Q_{z'}^2 R_{z'}^2).$$  \hspace{1cm} (7)

In order to apply this general expression to our specific case, we choose a reference frame (x', y', z') (attached to the sample) whose y' axis is the stretching direction as shown in Fig. 1. In this frame

$$Q_{x'} = Q_x$$
$$Q_{y'} = Q_y \cos \alpha$$
$$Q_{z'} = -Q_y \sin \alpha$$

where \( \alpha \) is the inclination angle, and \( \mathbf{Q} = Q(\cos \varphi, \sin \varphi, 0) \) is the scattering wave vector in the (x, y, z) frame attached to the detector. \( \varphi \) is the azimuthal angle of the scattering vector \( \mathbf{Q} \) relative to the x axis on the detector. Note also that

$$R_{x'}^2 = R_{x}^2$$
$$R_{y'}^2 = R_{y}^2$$
$$R_{z'}^2 = R_{z}^2/2$$

and, therefore,

$$X = Q^{*2} R^{*2}$$

with

$$R^{*2} = 3[(R_{x}^2/2)\sin^2 \alpha + R_{y}^2/2\cos^2 \alpha]$$
$$Q^{*2} = Q^2 + \varepsilon^2 Q_x^2$$
$$\varepsilon^2 = (R_{x}^2/2)/[(R_{x}^2/2)\sin^2 \alpha + R_{y}^2/2\cos^2 \alpha].$$  \hspace{1cm} (9)

A fit of the elliptically averaged SANS data to a form

$$I(Q^*) = A + BS(Q^*)$$  \hspace{1cm} (10)

yields a base line \( A \), an intercept \( B \) and an apparent radius of gyration \( R^*_g \).

III. Experiments

A polystyrene sample of 5% by weight perdeuterated polystyrene and 95% hydrogenated polystyrene was prepared by solvent blending. Gel-permeation chromatography measurements yielded (Hammouda, Bubeck & Mildner, 1986) \( M_w = 338000 \) and \( M_n = 239000 \) for the blend. The specimen was hot stretched at 283 K to an extension ratio of 1.5. The sample with a thickness of 1.5 mm was then mounted on an inclination device (as shown in Fig. 2) which allows its inclination angle \( \alpha \) to take on discrete values with an accuracy of 2°.

Data were taken on the University of Missouri Research Reactor SANS spectrometer (Mildner, Berliner, Pringle & King, 1981) in the following configuration: sample-to-detector matched path distance of 450 cm, source and sample aperture diameters of 2 and 1 cm respectively, and neutron wavelength of 4.75 Å, which yields reliable data in the range \( 0.007 < Q < 0.085 \) Å\(^{-1}\) with a resolution \( \Delta Q = 0.005 \) Å\(^{-1}\). A series of 8 h runs (at four different sample inclination angles) as well as a beam-open background (to correct for background scattering) were taken.

The two-dimensional SANS data were fitted to confocal ellipses in order to determine the eccentricity \( \varepsilon \) and orientation angle \( \varphi_0 \) of the elliptical iso-intensity contours for each run. This fitting was performed in the range \( 0.02 < Q < 0.03 \) Å\(^{-1}\) but was found not to vary much for other ranges. Given the extracted values for \( \varepsilon \) (shown in column 2 of Table 1), each entire SANS data set was elliptically averaged into bins of constant \( Q^* = (Q_x^2 + \varepsilon^2 Q_x^2)^{1/2} \) to give the function \( I(Q^*) \). A further fit of this intensity to a Debye function yields values for \( R^*_g \) which are presented in column 4 of Table 1. A test of the reliability of this fitting procedure can be obtained from the product \( \varepsilon R^*_g = (3/2)^{1/2} R_{x1} \) which should be independent of the inclin-
Table 1. Elliptical averaging of SANS data from a hot-stretched polystyrene sample tilted with respect to the scattering plane

The sample is a mixture of 5% perdeuterated with 95% hydrogenated polystyrene.

<table>
<thead>
<tr>
<th>Set inclination angle $\alpha$ (°)</th>
<th>Elliptical eccentricity $\varepsilon$</th>
<th>Average orientation angle $\alpha_0$ (°)</th>
<th>$R_\star^*$ (Å)</th>
<th>$\varepsilon R_\star^2$</th>
<th>Extracted $\alpha$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.52</td>
<td>88</td>
<td>231</td>
<td>120</td>
<td>0-0</td>
</tr>
<tr>
<td>30</td>
<td>0.56</td>
<td>90</td>
<td>204</td>
<td>114</td>
<td>32-6</td>
</tr>
<tr>
<td>45</td>
<td>0.63</td>
<td>90</td>
<td>187</td>
<td>118</td>
<td>43-0</td>
</tr>
<tr>
<td>60</td>
<td>0.78</td>
<td>91</td>
<td>149</td>
<td>116</td>
<td>62-1</td>
</tr>
</tbody>
</table>

In order to extract the inclination angle $\alpha$, the following transcendental equation is solved in each case:

$$(3/2)R_{\|}^2\sin^2\alpha + 3R_{\perp}^2\cos^2\alpha = R_\star^2.$$

The value used for $R_{\|}^2$ is obtained from the case $\alpha = 0$ as $3^{1/2}R_{\|}^2 = 231$ Å. Extracted $\alpha$ values are seen (column 6 of Table 1) to be close to the ‘true’ (set) values of column 1 to within 2 to 3°. This involves making measurements at one inclination angle and knowing the value of $3^{1/2}R_{\|}^2$ (obtained from $\alpha = 0^\circ$ for example), which is equivalent to taking SANS spectra at two (or more for better accuracy) different inclination angles. In Fig. 3, the extracted values for $R_\star^*$ are plotted vs $\cos^2\alpha$ where $\alpha$ represents the set inclination angle. A line can be fitted to this set of four points. The slope and intercept of this line yield $R_{\perp} = 93.1(46)$ and $R_{\|} = 133.0(39)$ Å. The extracted $R_\star^2$ values intersect the fitted line at $\alpha$ values which are reported in column 7 of Table 1 and are seen to be close to the values in column 6.

Note that there is a large uncertainty on the extracted angle for $\alpha = 0$ because the $\cos^2\alpha$ function is very flat close to $\alpha = 0$.

IV. Discussion

The formalism presented in this paper involves a few assumptions: (1) matched molecular weights of the perdeuterated and hydrogenated polymers, (2) no polydispersity corrections, (3) uncorrelated Gaussian distributions of the monomer interdistances in the directions parallel and perpendicular to the stretch axis, (4) uniform deformation of chain portions (i.e. $\varepsilon_x$, $\varepsilon_y$ and $\varepsilon_z$ are independent of $i$ and $j$) and, finally, (5) no multiple scattering because of the low sample thickness (1.5 mm). Note that for $\alpha = 60^\circ$ the effective thickness (traversed by the beam) of the sample is twice its real thickness. Although they are reasonable for the sake of extracting a solution, none of these assumptions is absolutely valid for a real system; they may all contribute to the discrepancies (a few %) between the extracted and true values of $\alpha$.

Our hot-stretched sample has been prepared in such a way that chains are oriented parallel to the surface. The technique discussed here could be valuable in cases where the symmetry axis of the nonisotropic inhomogeneities makes an (unknown) angle $\alpha_0$ with the surface of the sample. In this case, SANS spectra taken at two (or more) different inclination angles (for example, at $0^\circ$ corresponding to $\alpha_0$ and at $30^\circ$ corresponding to $\alpha_1 = \alpha_0 + 30^\circ$) are sufficient to extract the unknown value of $\alpha_0$. The solution of the system of equations

$$(3/2)R_{\|}^2\sin^2\alpha_0 + 3R_{\perp}^2\cos^2\alpha_0 = R_\star^2,$$

$$(3/2)R_{\|}^2\sin^2\alpha_1 + 3R_{\perp}^2\cos^2\alpha_1 = R_\star^2,$$

where $R_\star^2$, $R_{\|}^2$ and $R_{\perp}^2$ are obtained from the Debye fits to elliptically averaged data, yield the two unknown quantities $R_{\|}^2$ and $\alpha_0$.

It should be mentioned that optical birefringence and infrared dichroism have been extensively used [Sun, Kyu, Sheng, Lefebvre, Stein & Porter (1985) and Samuels (1981) among others] to investigate macromolecular orientation.
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References