polymer papers

Multiple scattering in small-angle neutron scattering measurements on polymers*

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Multiple scattering corrections in small-angle neutron scattering experiments on polymers have been examined. Numerical calculations show that, for typical experimental conditions, the second-order scattering is less than 2% of the first-order scattering for QR_g up to 10.0. An approximate expression is also given for obtaining a rough estimate of the second-order scattering without numerical calculation.

INTRODUCTION

Small-angle neutron scattering (SANS) measurements on samples consisting of mixtures of normal and deuterated polymers have been used for a decade to study the configuration of polymer chains in bulk[1-6] and in concentrated solutions[1,7]. The measured distributions in these experiments contain a finite contribution from neutrons which have suffered more than one scattering event in the sample. However, the effect of the multiply scattered neutrons have not been taken into account in published studies on polymer samples. It has not been certain whether these corrections are indeed small, particularly in experiments using the high concentration tagging technique[3-5]. In this paper, we report a calculation for the relative magnitudes of the second-order and the first-order scattering in SANS measurements on polymers.

The general problem of multiple scattering in neutron experiments was formulated by Vineyard[8] in 1954. This treatment has been used for calculating higher-order scattering events in wide-angle neutron scattering experiments[9-12]. To calculate multiple scattering effects in SANS experiments, Schelten and Schmatz[13] suggested a somewhat different procedure, which involves numerical evaluation of the Fourier transforms of the scattering functions. This was used for neutron scattering from spheres[13] where the coherent scattering function $\Sigma_{coh}(Q)$ varies rapidly (Q^{-4}) at large wavevector transfer Q. We have found that in the case of polymer chains, where $\Sigma_{coh}(Q)$ varies as Q^{-2} at large Q, the Fourier transform method results in significant truncation errors for practical limits of integration. We have, therefore, used Vineyard's formulation for the present calculations. The theory of the method is given in the next section. Results and discussion of the calculations are given in the third section. The fourth section gives an analytical expression

for obtaining a crude estimate of the second-order scattering. We summarize these results in the final section.

THEORY

We consider neutron scattering from an infinite slab of thickness t. A well collimated beam of neutrons of wavevector $\mathbf{k}_0$ and a uniform current density I_0 neutrons per square centimetre per second per steradian is incident along the normal to the flat surface of the sample. $\mathbf{k}$ is the wavevector of the neutrons that emerge from the sample and proceed towards the detector. $\mathbf{k}$ makes an angle θ with the slab normal as shown in *Figure 1*. In general, the neutrons might be scattered in the specimen several times
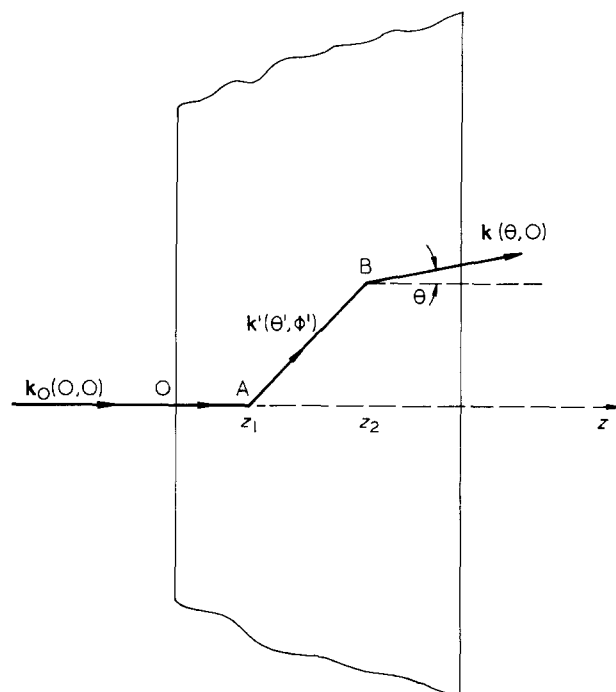

Figure 1 Scattering geometry for the two scattering situation. $\mathbf{k}_0$, $\mathbf{k}$ and the slab normal are in $\phi=0$ plane. Direction of $\mathbf{k}'$ is given by polar angles (θ', ϕ')

before they emerge. In the following, we obtain the expression for the second-order scattered neutron current $I_2(Q)$ as a function of the wavevector transfer $Q(=k_0-k)$ using an approach similar to that developed by Vineyard[8] and later workers[9-12].

Let us assume that the two scattering events occur at A and B respectively (*Figure 1*). The incident neutron is first elastically scattered at A and proceeds along k'. It suffers a second elastic scattering at B and emerges from the sample in the direction of k. To describe the trajectory of the neutron, we use a spherical coordinate system with its pole along the inward slab normal. The polar angles (θ', ϕ') and (θ, ϕ) give the directions of k' and k respectively. We assume that the incident beam is well collimated such that k_0 has angles $(0, 0)$. We assume $I_2(Q)$ along (θ, ϕ) to be independent of the azimuthal angle ϕ. It is thus convenient to choose k_0, k and the slab normal to be coplanar and to measure the azimuthal angle ϕ from this plane. That is, we assume $\phi = 0$. If A and B are situated at depths z_1 and z_2 from the flat surface of the sample and if one assumes that both of the scatterings are forwards ($\theta, \theta' < \pi/2$), then it can be shown[8,12] that

$$I_2(Q) = I_0 \int_0^{\pi/2} d\theta' \sin\theta' \int_0^{2\pi} d\varphi' \left(\int_0^t dz_1 \sec\theta' e^{-\mu z_1} \Sigma(\theta') \right)$$

$$\times \int_{z_1}^t dz_2 \sec\theta\, e^{-\mu(z_2-z_1)\sec\theta'} \Sigma(\beta)\, e^{-\mu(t-z)\sec\theta} \right) \quad (1)$$

Here μ is the attenuation coefficient which includes absorption and all scattering processes including small-angle coherent scattering (SACS). $\Sigma(\theta)$ is the macroscopic differential scattering cross-section for the neutrons to be scattered through an angle θ. In the present problem, the scattering angle at first scattering is θ' and that at second scattering is β such that

$$\cos\beta = \cos\theta'\cos\theta - \sin\theta'\sin\theta\cos\phi' \quad (2)$$

Equation (1) can be simplified to obtain

$$I_2(Q) = 2I_0 e^{-\mu t} \int_0^{\pi/2} \Sigma(\theta') f_2(\theta,\theta') \sin\theta'\, d\theta' \int_0^{\pi} \Sigma(\beta) d\varphi' \quad (3)$$

where

$$f_2(\theta,\theta') = \frac{\sec\theta\sec\theta'}{\mu(\sec\theta' - \sec\theta)} \left(\frac{e^{-\mu t(\sec\theta'-1)}-1}{\mu(\sec\theta'-1)} - \frac{e^{-\mu t(\sec\theta-1)}-1}{\mu(\sec\theta-1)} \right) \quad (4)$$

It can be shown in a similar way that the first-order current $I_1(Q)$ emerging from the sample in the direction of k is given by

$$I_1(Q) = I_0 e^{-\mu t} \Sigma(\theta) f_1(\theta) \quad (5)$$

where

$$f_1(\theta) = \frac{\sec\theta(1-e^{-\mu t(\sec\theta-1)})}{\mu(\sec\theta-1)} \quad (6)$$

In SANS experiments on polymers, neutron scattering is dominated by SACS events. In general, there may also be a small contribution to $\Sigma(\theta)$ from incoherent scattering; we discuss this effect in the next section. For the present, we assume $\Sigma(\theta) = \Sigma_{coh}(\theta)$ only. This is determined by the configuration of the polymer chain and by the overall density fluctuations in the sample[3].

CALCULATION DETAILS AND RESULTS

It has been seen from equation (3) that, to calculate the second-order scattering corrections, one has to know $\Sigma_{coh}(\theta)$, the quantity one wants to measure. In principle, one can obtain $\Sigma_{coh}(\theta)$ and $I_2(Q)$ from the measured distribution using an iterative procedure if the higher-order scatterings are negligible. This requires a knowledge of $\Sigma_{coh}(\theta)$ over a large region of θ. In general, the measured distributions are not accurate at large θ. In view of this, we calculate instead the relative magnitudes of $I_2(Q)$ and $I_1(Q)$ using a model for the scattering function $\Sigma_{coh}(\theta)$. For the present purpose, we shall assume the polymer chains to be Gaussian (Debye model[14]). The effect of the density fluctuations on $\Sigma_{coh}(\theta)$ is normally small for bulk amorphous polymers, particularly for bulk polystyrene[4]; and we neglect this contribution. Then for a mixture of normal and deuterated polymer, it can be shown[3] that

$$\Sigma_{coh}(\theta) = \frac{2C}{p^2}(p - 1 + e^{-p}) \quad (7)$$

where

$$C = (a_H - a_D)^2 N n^2 \chi(1-\chi)$$

and

$$p = (2k_0 \sin\tfrac{1}{2}\theta)^2 R_g^2 = Q^2 R_g^2$$

Here R_g is the radius of gyration for the polymer chain. a_H and a_D are the coherent scattering lengths per protonated and deuterated monomer respectively. N is the number of polymer chains per unit volume of the sample and n is the number of monomers in each chain. χ is the number fraction of monomers that are deuterated in the sample. We use this model for all coherent elastic scattering events. While equation (7) is incorrect for large Q, and hence large scattering angles, the error is made negligible by the rapid reduction in $\Sigma_{coh}(\theta)$ as θ increases.

The first- and second-order scatterings $I_1(Q)$ and $I_2(Q)$ have been numerically computed using equations (3)–(7) for bulk polystyrene samples of molecular weight $M_w = 194\,000$, $t = 0.12$ cm and $\chi = 0.3$ corresponding to typical high concentration sample conditions[4]. R_g for a polystyrene chain of molecular weight M_w is equal to $M_w^{1/2}$ times a well established constant[2,4,6]. That is

$$R_g = 0.267 M_w^{1/2}$$

k_0 was taken to be 1.323 Å^{-1}. The integrations in equation (3) were carried out numerically on the θ' range $[0, \theta'_{max}]$ and simultaneously in the ϕ' range $[0, \pi]$. The restriction on θ'_{max} shortens the computation time and introduces only an insignificant error because $\Sigma_{coh}(\theta')$ becomes negligibly small at large angles. Calculations for $I_2(Q)$ have been made for θ'_{max} varying from $\pi/25$ up to
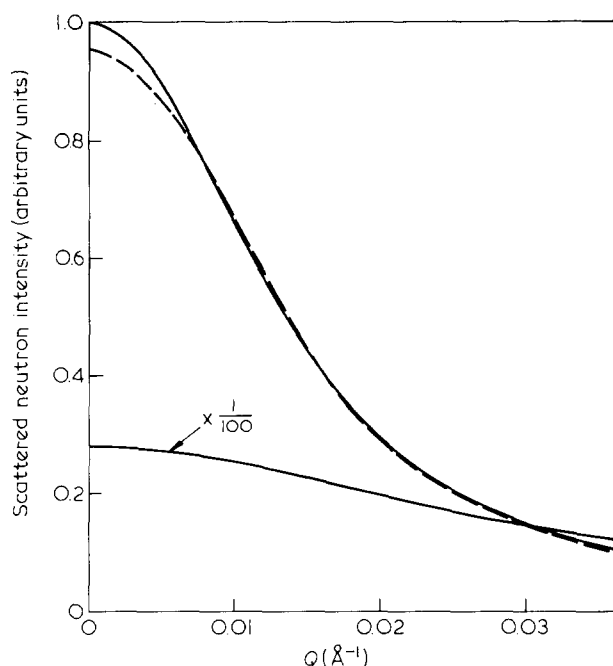
Figure 2 Scattered neutron intensity *versus* Q for the Debye chains. The upper and lower full curves are numerically calculated $I_1(Q)$ and $I_2(Q)$ using Vineyard's method as discussed in the text. The broken curve is the *total* scattering $I(Q)$ calculated using the method of Schelten and Schmatz

$\pi/10$ and show constant results within 2%. The results shown in *Figure 2* correspond to $\theta'_{max} = \pi/15$. In this figure, the upper and lower full curves correspond to $I_1(Q)$ and $I_2(Q)$ respectively (note a factor $1/100$ for $I_2(Q)$). This gives a ratio of $I_2(Q)/I_1(Q)$ in the range of about 0.28 to 1.2%. In view of this result, the third-order scattering is expected to be negligible[8].

In these calculations, we have assumed the neutron scattering to be purely coherent. Incoherent scattering is not negligible for a sample consisting of a mixture of normal and deuterated polymers. While $\Sigma_{coh}(\theta)$ decreases with increase in θ, the incoherent scattering cross-section $\Sigma_{inc}(\theta)$ remains approximately constant. For the experimental situation under discussion, $\Sigma_{inc}(0)/\Sigma_{coh}(0) \simeq 0.005$ in the forward direction and $\Sigma_{inc}(\theta)$ is larger than $\Sigma_{coh}(\theta)$ for $\theta > \pi/15$. In view of this, one expects the total second-order scattering $I'_2(Q)$ to consist of three parts $I^a_2(Q)$, $I^b_2(Q)$ and $I^c_2(Q)$ arising from three types of scattering events: (a) two coherent scattering events, (b) one coherent and one incoherent scattering event, and (c) two incoherent scattering events. The second-order scattering curve shown in *Figure 2* corresponds to $I^a_2(Q)$. Calculations similar to the one described above were carried out using

$$\Sigma(\theta) = \Sigma_{coh}(\theta) + \Sigma_{inc}(\theta)$$

These calculations gave a second-order intensity which was about 5% larger than that shown in *Figure 2*. We believe this extra intensity corresponds to $I^b_2(Q)$. We need not calculate $I^c_2(Q)$ as it is removed by the experimental procedure of subtracting the scattering from a control sample from the total scattering of the marked sample. This approximately corrects the data for multiple incoherent scattering also. In view of the above discussion, the effect of the incoherent scattering on the

present calculations is ignored. We assume $I^a_2(Q) = I'_2(Q) = I_2(Q)$. It is seen that multiple scattering corrections are quite small. The radius of gyration R_g obtained from the uncorrected data is expected to be accurate to 1%.

It should be noted that if the same problem is tested using the method of Schelten and Schmatz[13], the second-order scattering term $I_2(Q)$ is comparable to within 5% of that shown in *Figure 2*. However, the *total* scattering

$$I(Q) = \sum_{n=1}^{\infty} I_n(Q)$$

is significantly different as shown by the broken curve of *Figure 2* and leads to an apparent change in R_g of about 10%. This is because $I(Q)$ suffers from large truncation errors even when the limits of integration in the numerical evaluation of the Fourier transforms were taken to be 1.5 times larger than those used by Schelten and Schmatz. Oscillations in the calculated $I(Q)$ were also seen. We believe this is because of the slow (Q^{-2}) decrease in $\Sigma_{coh}(Q)$ with Q for the polymer chains. The Schelten and Schmatz calculation is for spheres and because of the Q^{-4} dependence does not suffer from truncation errors.

ANALYTICAL EXPRESSION FOR SECOND-ORDER SCATTERING

An analytical expression for the second-order scattering $I_2(Q)$ has been obtained following the treatment of Schelten and Schmatz but approximating the true form of $\Sigma_{coh}(Q)$ by a Lorentzian function of the form

$$\Sigma_{coh}(Q) = \frac{C}{1 + Q^2 R_g^2/3} \tag{8}$$

This is a reasonable approximation to the Debye equation (7). Schelten and Schmatz showed that

$$I_n(Q) = \frac{I_0}{2\pi} \int_0^{\infty} J_0(Qr) h_n(r) r \, dr \tag{9}$$

where

$$h_n(r) = \frac{k_0^2}{n!} \left(\frac{s(r)}{k_0^2}\right)^n e^{-\mu t}$$

and $J_0(Qr)$ is a Bessel function of zero order. $s(r)$ in the above expression is given by

$$s(r) = 2\pi \int_0^{\infty} J_0(Qr) \Sigma_{coh}(Q) t Q \, dQ \tag{10}$$

Using equations (8), (9) and (10), it can be shown that

$$I_2(Q) = \frac{9\pi I_0 C^2 t^2 e^{-\mu t}}{R_g^2 k_0^2} F(QR_g) \tag{11}$$

where

$$F(QR_g) = F(p) = \frac{1}{p^{1/2}(12+p)^{1/2}} \ln\left(\frac{(12+p)^{1/2} + p^{1/2}}{(12+p)^{1/2} - p^{1/2}}\right)$$
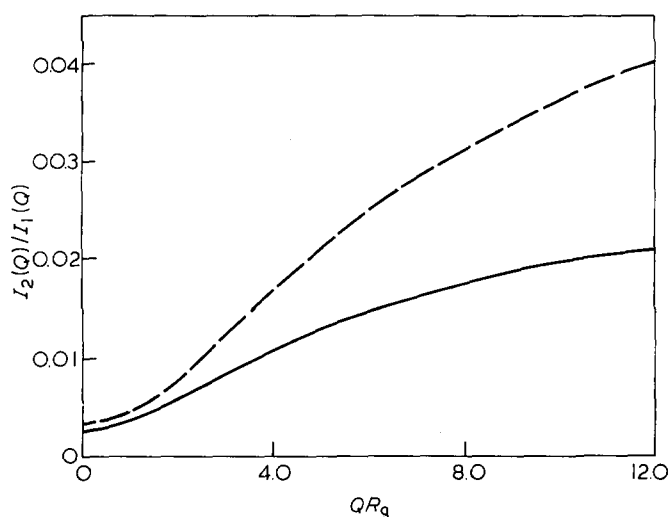
Figure 3 $I_2(Q)/I_1(Q)$ as a function of QR_g. For the full curve, $I_2(Q)$ is that for the Debye chains and was obtained numerically using equation (3). For the broken curve, $I_2(Q)$ was obtained from the analytical expression (11). For both curves $I_1(Q)$ was obtained using equation (7) (Debye model)

A comparison of this expression* with the numerical results of the previous section is shown in *Figure 3* for $M_w = 10^6$. The broken and full curves correspond to analytical and numerical results, respectively. Here, instead of $I_2(Q)$, we have plotted $I_2(Q)/I_1(Q)$ as a function of QR_g—and have used the same $I_1(Q)$ (equation (7)) for both the curves. It is seen that compared to the numerical results equation (11) gives 25 to 90% higher $I_2(Q)$. The curve is also valid for lower molecular weights and can be used for estimating the relative magnitudes of the second- and first-order scatterings for polymer samples.

SUMMARY

The relative magnitudes of the second-order and the first-order scatterings in SANS experiments on mixtures of

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* Equation (11) gives $I_2(Q)$ identical to the one obtained numerically using equation (3) with a Lorentzian function for $\Sigma_{coh}(Q)$.

normal and deuterated polymers have been calculated numerically using Vineyard's method. The calculations for 0.12 cm thick samples of bulk polystyrene, containing 30% deuterated chains, show that the second-order scattering is less than 2% of the first-order scattering up to $QR_g = 10.0$. The second-order scattering is expected to be smaller when the concentration of the tagged chains is smaller. Consequently, we believe that the multiple scattering corrections in SANS experiments on polymers are normally quite small.

An approximate expression for obtaining the second-order scattering is also given. A comparison of this expression with the numerical results shows that it overestimates the second-order scattering. This expression may be considered a conservative upper limit of the second-order scattering in SANS experiments on polymers and does not require numerical calculation.

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