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## Hydrogen momentum distribution in anisotropic rigid-chain polymers

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**Abstract.** We have performed a trial deep inelastic neutron scattering (DINS) experiment on an aligned sample of a copolymer of poly(hydroxybenzoic acid) and poly(hydroxynaphthoic acid). The experiment has been carried out on the eVS inelastic spectrometer of the ISIS facility, at the Rutherford Appleton Laboratory (UK). The hydrogen atomic momentum distributions  $n_{\parallel}(p)$  and  $n_{\perp}(p)$ , corresponding to momentum transfer  $Q$  parallel and perpendicular to the polymer main chain direction respectively, have been obtained as functions of the atomic momentum  $p$ . The experiment offers evidence of the insensitivity of the DINS technique to the degree of rigidity of the polymer main chain. Through the use of a quantum mechanical model we show that the hydrogen momentum distribution is defined by the C-H bond and that bonds connected to the carbon or other interactions have no significant influence.

### 1. Introduction

Polymer molecules are intrinsically anisotropic. The covalent bonding along the chain can result in materials with exceptionally high mechanical moduli, if the chains are organized to be straight and with a high level of preferred orientation [1]. Of course for many polymer systems the entropically driven random coil configurations inhibit the generation of highly anisotropic materials. Recently, considerable efforts have been made to design new materials and new routes to such highly organized molecular materials.

Among all the experimental techniques that can be used to investigate anisotropy in polymers, deep inelastic neutron scattering (DINS) is unusual in that it probes the response of the material on a very local, i.e. atomic scale.

The technique provides a means of determining the ground state momentum distribution of a system. The procedures, which are sometimes referred to as neutron recoil scattering, are similar to inelastic photon scattering, which is used to determine the electron momentum distribution.

DINS is still in its infancy, principally due to the restrictions that the experiment needs to be performed with high-energy neutrons and at large momentum transfer  $Q$ . High-energy neutrons are necessary to observe the momentum distribution of the recoiling atoms. Large momentum transfers are needed in order to have atoms recoiling with a kinetic energy much greater than the potential energy of the neighbouring atoms, so that the atoms can be regarded as essentially free. This last

condition, known as the impulse approximation, provides a simple and direct relationship between the measured incoherent scattering function,  $S(\mathbf{Q}, \omega)$ , and the atomic momentum distribution  $n(\mathbf{p})$ ,  $\mathbf{p}$  representing the atomic momentum.

With the advent of accelerator-based pulsed neutron sources [2], high fluxes of epithermal neutrons are now available, which allow measurements to be performed at sufficiently high  $Q$  to satisfy the impulse approximation [3, 4].

The objective of this study was to obtain information on the local environment experienced by the polymer chain by performing measurements on a sample with a high level of preferred orientation. By using samples with high levels of preferred molecular orientation, the experiment directly provides the momentum distribution of some particular atom in the system (in this case the hydrogen atom) in directions parallel and perpendicular to the axis of the polymer chains.

The availability of such microscopic information would provide invaluable data to be compared with and related to macroscopic mechanical and other properties.

## 2. Theory of DINS

The outcome of a neutron inelastic scattering experiment is the scattering differential cross section:

$$\frac{d^2\sigma}{d\Omega d\omega} = Nb^2 \frac{k_f}{k_i} S(\mathbf{Q}, \omega) \quad (1)$$

where  $N$  is the number of scattering units,  $b$  is the scattering length,  $k_i$  and  $k_f$  are the initial and final neutron wavevector and  $S(\mathbf{Q}, \omega)$  is the dynamic structure factor.

The impulse approximation [5] relates  $S(\mathbf{Q}, \omega)$  to the atomic momentum distribution  $n(\mathbf{p})$  as follows [4, 6-8]:

$$S(\mathbf{Q}, \omega) = \frac{1}{\hbar} \int n(\mathbf{p}) \delta\left(\hbar\omega - \frac{\hbar Q^2}{2M} - \frac{\hbar\mathbf{p} \cdot \mathbf{Q}}{M}\right) d\mathbf{p} \quad (2)$$

where  $\hbar\omega$  and  $\hbar Q$  are the energy and momentum transfer in the scattering process,  $\hbar\mathbf{p}$  is the atomic momentum and  $M$  the atomic mass.

If the  $z$  axis is taken along the direction of  $\mathbf{Q}$ , then (2) reduces to:

$$S(\mathbf{Q}, \omega) = \frac{M}{\hbar Q} \int \delta(Y - \hbar p_z) n(\mathbf{p}) d\mathbf{p} \quad (3)$$

where

$$Y = (M/Q)(\omega - \hbar Q^2/2M) \quad (4)$$

After performing the integration over  $p_z$ , equation (3) assumes the form

$$S(\mathbf{Q}, \omega) = (M/\hbar Q) J(Y) \quad (5)$$

where

$$J(Y) = \int n(p_x, p_y, Y) dp_x dp_y. \quad (6)$$

$J(Y)$  is the so-called 'Compton profile', which determines the probability that an atom has momentum component  $Y$  along the direction of  $Q$  (equation (6)).

Since  $J(Y)$  has its maximum value at  $Y = 0$ , for a given  $Q$   $S(Q, w)$  is maximum at  $w = w_R = \hbar Q^2/2M$ . Furthermore, the width of  $S(Q, w)$  is  $2\hbar Q \Delta p/M$ , where  $\Delta p$  is the width of the  $n(p)$  distribution.

If  $n(p)$  does not depend on the direction of  $p$ , integration over the angle between  $p$  and  $Q$  leads to

$$S(Q, w) = \frac{2\pi M}{\hbar Q} \int_{|Y|}^{\infty} pn(p) dp \quad (7)$$

and  $n(p)$ , the quantity of physical interest, can be obtained from the derivative of the experimentally determined  $S(Q, w)$ .

It should be noted that any measurement of  $S(Q, w)$  at constant  $Q$  completely determines the Compton profile. Thus a complete determination of  $S(Q, w)$  is not necessary for a measurement of  $J(Y)$ ; all that is required is a single scan across the recoil peak at constant  $Q$ .

Detectors placed at different positions collect scattered neutrons corresponding to different  $Q$  directions. If the sample of interest is characterized by a certain global anisotropy, then the different detectors provide, in principle, a route to obtaining simultaneously the hydrogen momentum distribution in different directions with respect to the sample anisotropy axis. In particular, if a sample with uniaxial symmetry is placed in the beam at a  $45^\circ$  angle with respect to the incident neutron beam direction, the spectra collected at scattering angles of  $-45^\circ$  and  $+45^\circ$  give the atomic momentum distributions  $n_{\parallel}(p)$  and  $n_{\perp}(p)$  corresponding to  $Q$  parallel and perpendicular to the anisotropy direction respectively.

### 3. Material

The polymer under investigation is a main-chain thermotropic copolyester which was supplied by ICI Plc. It is a random copolymer of hydroxybenzoic and hydroxynaphthoic acids, in number fractions of 0.58 and 0.42 respectively. Figure 1 shows its chemical composition.

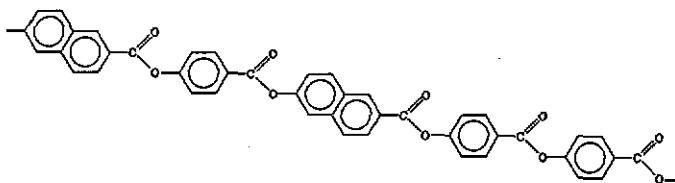


Figure 1. A representative section of the random copolymer (HBA/HNA)<sub>58/42</sub> used in these experiments. The naphthoic and benzoic units are distributed randomly along the chain.

The molecule is relatively rigid. It was obtained in the form of extruded pellets. Previous x-ray diffraction experiments [9] have shown that there is a marked alignment of the molecular chain axis with the extrusion axis, that the orientation distribution is

symmetrical about this axis and that the degree of molecular orientation is uniform across the section normal to the axis.

In such a structural configuration, the C-H bonds of interest in our experiment can therefore be considered perpendicular to the main-chain direction.

Although this sample may appear to be complex in that it lacks crystalline order, it does provide simplification through the high level of disorder and hence 'equivalence' of the atomic sites.

#### 4. Experiment

The DINS experiments were performed on the Electron Volt Spectrometer (eVS) at the ISIS pulsed neutron scattering facility at the Rutherford Appleton Laboratory.

eVS is an inverse geometry inelastic spectrometer, which utilizes an unconventional filter difference technique to analyse the energy of the scattered neutrons [4, 6]. Conventional analysers such as choppers or crystal analysers are in fact inefficient at the discrimination of energies in the epithermal region. The technique relies on the usage of well defined narrow nuclear resonances that exist in this energy region. In particular, the resonances currently used on eVS are respectively 6600 meV from uranium and 4906 meV from gold. The latter is adequate for the study of recoil scattering from hydrogen.

The resonance analysers are in the form of thin foils. The scattered spectrum is obtained as the difference of the signals collected with the resonance filter in and out of the beam respectively.

Four  $^3\text{He}$  detector banks collect the recoil spectrum at angles of  $\pm 45^\circ$  and  $\pm 135^\circ$ .

Two experiments have been performed, in which the sample, contained in an aluminium flat-plate container, has been arranged such that the axes of the main polymer chain were aligned in directions either parallel or perpendicular to the container surface. In both of the experiments, the sample has been positioned in the spectrometer at an angle of  $45^\circ$  with respect to the direction of the incident neutron beam. Figure 2 shows a schematic diagram of the chosen experimental geometry.

In this geometry, by analysing separately the spectra collected at the detector banks positioned at  $-45^\circ$  (bank A) and  $+45^\circ$  (bank B), it was possible, in principle, to obtain  $n_{\parallel}(p)$  and  $n_{\perp}(p)$  simultaneously from a single experiment.

In practice, due to the chosen conditions, the effects of multiple scattering were expected to be significant, and indeed they turned out to be quite severe for the spectra collected at detector bank B. As a consequence, the resulting momentum distribution from the latter detectors is rather asymmetric and difficult to study. Therefore, in the following analysis, we have been considering the data from detectors A only, from both the experiments.

The 4.906 eV Au resonance analyser has been used to analyse the energy of the scattered neutrons, allowing the study of energy transfers between 10 and 30 eV and momentum transfers greater than  $100 \text{ \AA}^{-1}$ .

In this configuration, the instrumental resolution in momentum space has a Lorentzian bandshape, whose width  $\Delta p$  is dependent on the scattering angle  $\theta$ ; for the scattering angles we have considered in the analysis,  $\Delta p$  varies between 1.2 and  $2.2 \text{ \AA}^{-1}$ .

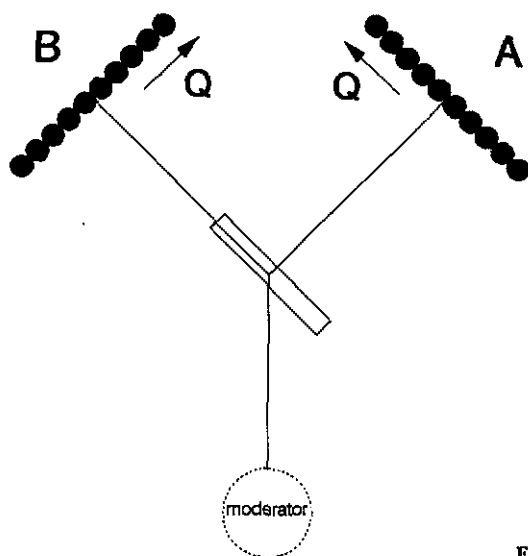


Figure 2. Geometry of the experiment.

## 5. Data presentation

The validity of the impulse approximation for our experiment has been checked by testing the linearity in the behaviour of the recoil energy  $E_R = \hbar\omega_R$  as a function of  $Q^2$ , as seen in section 2. Figure 3 shows a typical example of the results obtained: the impulse approximation is clearly satisfied.

The momentum distributions  $n_{\parallel}(p)$  and  $n_{\perp}(p)$  as a function of  $p$  were derived from each time-of-flight (TOF) spectrum at every scattering angle [6],\* for the ten detectors in bank A ( $35^\circ \leq \theta \leq 55^\circ$ ). For the purpose of analysis these spectra were merged and figure 4 shows the results obtained. As can be seen, the anisotropy in the momentum distribution is very small, indeed much smaller than first expected.

## 6. Model

The experimental results were found to be in agreement with a rather simple model, which is described in detail in the following.

Assume that the polymer main chain is rigid [9] and, as mentioned earlier, that the C-H bond lies perpendicular to the main-chain direction. We have taken into consideration the two main vibrational motions characteristic of the C-H bond in an aromatic group, i.e. bond stretching and out-of-plane bending.

$n_{\parallel}(p)$  will contain information on the bending motion only, the stretching vibration being spatially confined in the direction of the bond.

The hydrogen wavefunction corresponding to the experimental  $n_{\parallel}(p)$  can therefore be modelled with the solution to the Schrödinger equation for an oscillator in a harmonic potential well. The ground state energy and wavefunction are given by the relations [8]

$$E = \frac{1}{2}\hbar\omega_b \quad \psi(x) = (m\omega_b/\pi\hbar)^{1/4} \exp(-m\omega_b x^2/2\hbar)$$

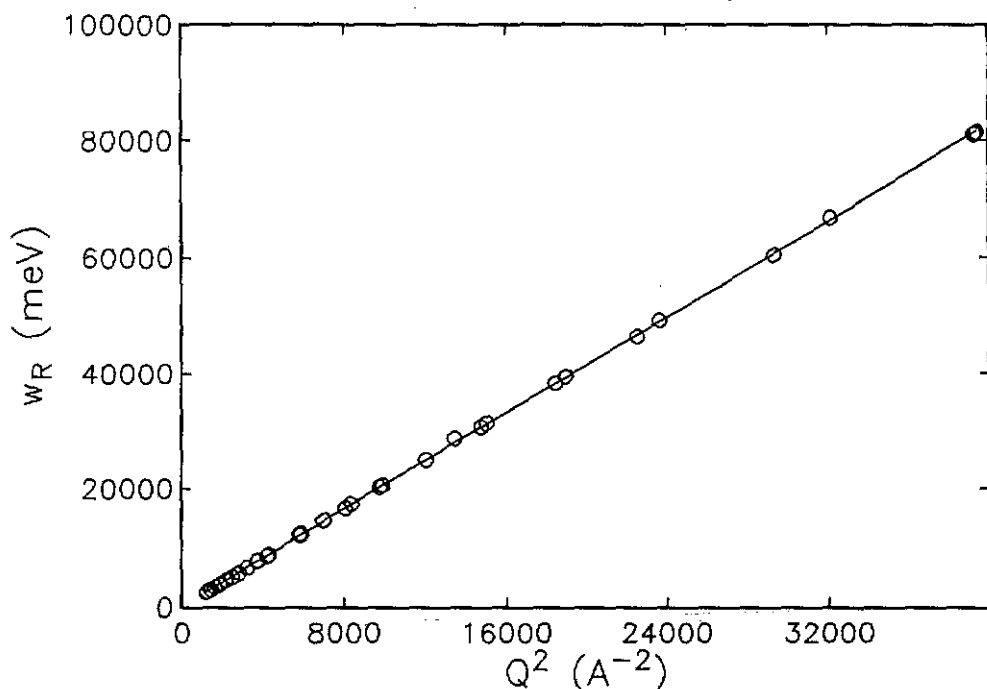


Figure 3.  $E_R$  versus  $Q^2$ . Circles are experimental results; the continuous line is the best fit. From the slope of the line the value  $M = 1.033$  is obtained for the hydrogen mass.

where  $\omega_b$  is the characteristic bending vibration frequency and  $m$  the oscillator mass. All the excited states of the oscillator can be ignored, since  $k_B T \ll \hbar \omega_b$ . An expansion of  $\psi(x)$  in terms of momentum eigenfunctions

$$\psi(x) = \sum_p a(p) \exp(ipx/\hbar) \quad (8)$$

leads to the following expression for the expansion coefficients:

$$a(p) = 2(\pi\hbar/m\omega_b)^{1/4} \exp(-\hbar p^2/2m\omega_b) \sim \exp(-kp^2/\omega_b) \quad (9)$$

where  $k = \hbar/2m$  and  $a(p)$  is the probability amplitude for momentum  $p$ . The momentum distribution satisfies the following relationship:

$$n_{\parallel}(p) = [a(p)]^2 \sim \exp(-2kp^2/\omega_b) \quad (10)$$

and  $n_{\parallel}(p)$  therefore has a Gaussian form.

On the other hand, the scattering with  $Q$  parallel to the bond direction will be modulated both by the stretching vibration and by a component of the bending motion.

The harmonic oscillator is in this case a bidimensional one. If the vibrational motion is taking place in the  $xy$  plane, the probability amplitude assumes the expression

$$A(p_x, p_y) = a(p_x)a(p_y) = \exp(-k(p_x^2/\omega_s + p_y^2/\omega_b)) \quad (11)$$

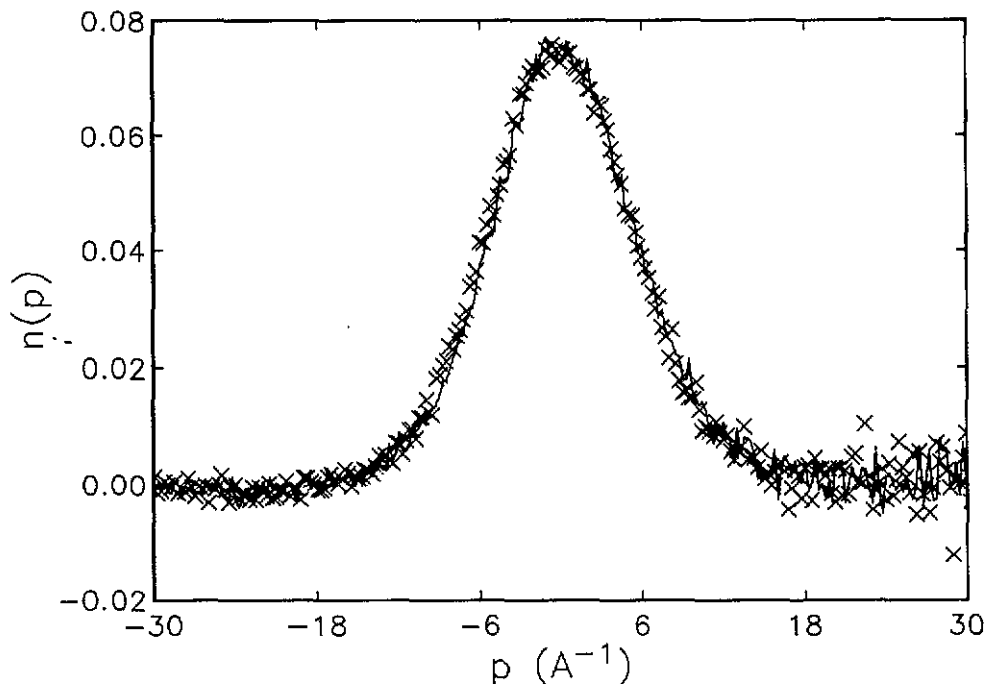


Figure 4.  $n_{\parallel}(p)$  (crosses) and  $n_{\perp}(p)$  (line) as functions of  $p$ .

where  $w_s$  is the C-H stretching characteristic frequency and  $p_x$  and  $p_y$  are the components of  $p$  along the two axes of the  $xy$  plane.

Equation (10) is then modified in the following way:

$$n_{\perp}(p) \sim \exp(-2k(p_x^2/w_s + p_y^2/w_b)). \quad (12)$$

Furthermore, in this geometry the scattering will be sensitive to the motions of a distribution of bonds in the  $xy$  plane. The observed momentum distribution is therefore an average of  $n_{\perp}(p)$  over all possible orientations for the C-H bond. After calculation, equation (12) becomes

$$\langle n_{\perp}(p) \rangle \sim \exp(-kp^2(1/w_s + 1/w_b)) I_0(kp^2(1/w_b - 1/w_s)) \quad (13)$$

where  $I_0$  is the modified Bessel function of order 0.

We have performed a fit of the experimental  $n_{\parallel}(p)$  and  $n_{\perp}(p)$ , using expressions (10) and (13) respectively, which have been convoluted with a Lorentzian function of width  $1.5 \text{ \AA}^{-1}$ , representing the average instrumental resolution function in momentum space for the group of detectors in bank A. The variable parameters of the fit were the frequencies  $w_b$  and  $w_s$  and a multiplicative factor that adjusted the overall intensity of the model peak to the experimental results, which are on an arbitrary scale.

Figure 5 shows the best fit of  $n_{\parallel}(p)$ , obtained with the single gaussian of expression (10). The corresponding value for the characteristic bending vibrational frequency is  $w_b = 1586 \pm 46 \text{ cm}^{-1}$ , in good agreement with results from infrared spectroscopy investigations (see, e.g., [10]).



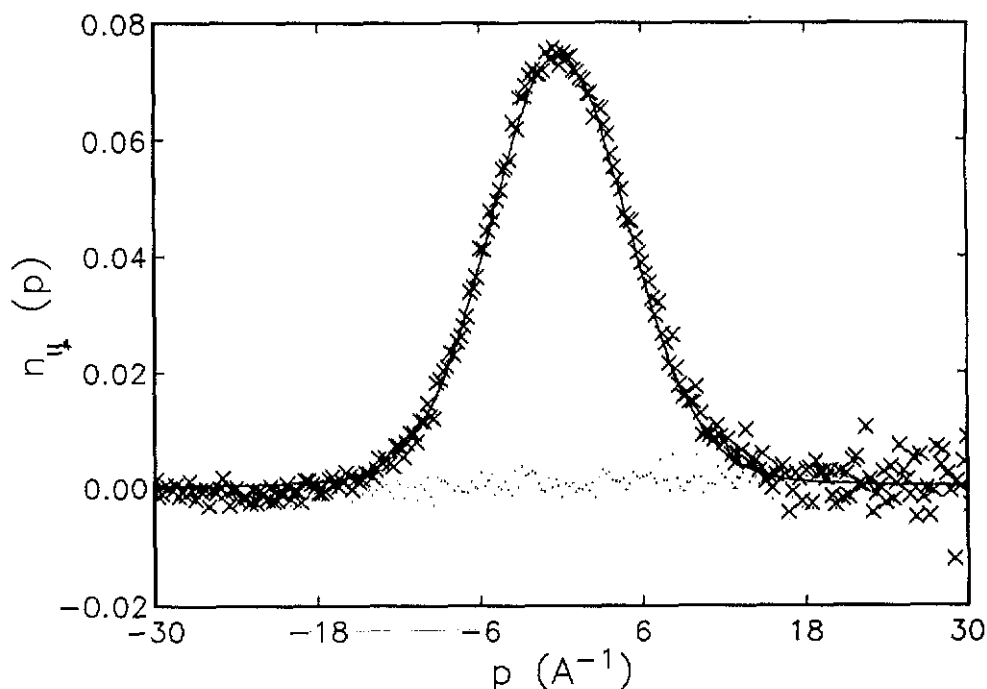


Figure 5. A model fit to  $n_{\parallel}(p)$ , using a convolution of (10) with a Lorentzian resolution function. Crosses: experimental results; solid line: best fit; dotted line: difference.

Although the lineshape of  $n_{\perp}(p)$  seems at first sight to be satisfactorily represented by a single gaussian, the quality of such a fit is not as good as that obtained for  $n_{\parallel}(p)$ . By choosing instead to interpret the experimental  $n_{\perp}(p)$  in terms of the model described (equation (13)), using for  $w_b$  the value determined from the fit to  $n_{\parallel}(p)$ , we succeed in obtaining a very good representation of the experimental results, as figure 6 shows. The value of the best-fit frequency for the stretching vibration is  $w_s = 3174 \pm 93 \text{ cm}^{-1}$ , which again is in remarkable agreement with IR results [10]. Furthermore it is to be noted that the sensitivity of the model fit to the variation of the parameters is quite high. In particular, an attempt at fitting  $n_{\perp}$  with expression (12) alone, without taking into consideration the higher-order term represented by the Bessel function  $I_0$ , gives a poor fit of the experimental peak shape, indicating the importance of averaging over all possible orientations of the C-H bond.

Two independent experiments on the same material gave consistent values for  $w_b$  and  $w_s$ , within experimental error.

## 7. Conclusions

DINS is an interesting novel technique for studying atomic momentum distributions in the condensed phase. In particular, it gives information on the hydrogen wavefunction, whereas conventional neutron spectroscopic techniques only allow information to be obtained on energy eigenfunctions.

A few previous works [11, 12] have shown the usefulness of the technique in the study of anisotropic materials.

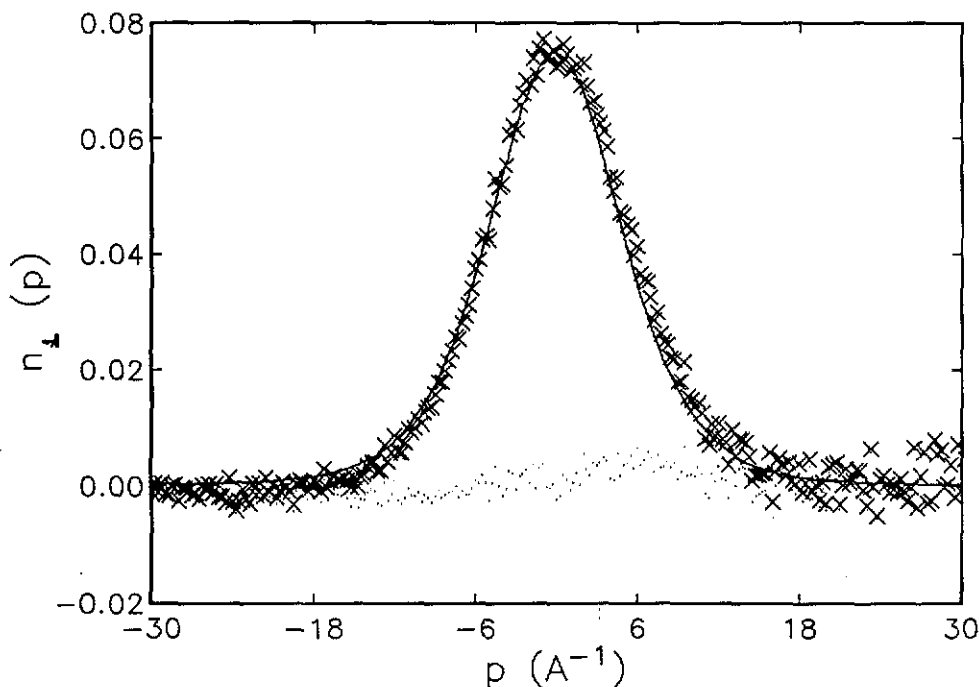


Figure 6. As figure 5, but for  $n_{\perp}(p)$ , using (13).

In our experiment, a simple quantum mechanical model, which takes into consideration the coupling of neutrons with the limited types of motion of the hydrogen atom in the polymeric system of interest, has been successful in describing the small difference observed between the hydrogen atomic momentum distributions obtained for directions respectively parallel and perpendicular to the symmetry axis of the sample.

Nevertheless, the real scope of our experiment has not been fulfilled.

Our original aim was in fact to use  $n_{\parallel}(p)$  and  $n_{\perp}(p)$  as indirect probes of the degree of stiffness of the polymer main chain. Our expectation was that the polymer chain would have a major influence on the anisotropy in the potential experienced by the hydrogen atom. Ultimately, this was expected to lead to different proton recoil scatterings depending upon the relative directions of the momentum transfer and the C-H bond.

The experiment performed shows instead that all the information gained is on the relevant motions of the C-H bond, but that nothing can be concluded regarding the molecular organization, and in particular the degree of structural anisotropy, surrounding the proton whose recoil is monitored. In other words, the influence of the chain environment is restricted to the single covalent C-H bond and does not apply to other bonds nor to the Van der Waal interactions.

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