

NEUTRON SCATTERING STUDIES OF SELF DIFFUSION IN RUBBERS AND POLYMER MELTS

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ABSTRACT

Neutron incoherent scattering studies of simple liquids reveal that the classical translational motion of the molecules gives rise to a Doppler broadening of the elastic peak. From the band-width at half-peak height, measured as a function of momentum transfer, the self-diffusion coefficient can be obtained for the translational motion of the molecules. Experiments on oligomers and high polymers of dimethylsiloxane show similar results, as do measurements of poly(propylene oxide), polyisobutylene and poly(ethylene oxide). Measurements on partially deuterated samples confirm that the effect arises from segmental diffusive motion, rather than rotations of pendant side-groups. The temperature dependence of this motion gives activation energies which are smaller than the activation energies for self-diffusion obtained from experiments of longer time-scale such as nuclear spin-lattice relaxation measurements and viscometry.

The chemical applications of thermal neutron scattering are reviewed *in extenso* in a recent book¹. Both inelastic and elastic processes are useful. Elastic scattering experiments are closely analogous to experiments carried out in the field of x-ray crystallography; they yield information on the structure of crystals and also on the atomic magnetic moments in the materials. Inelastic scattering experiments give information about the dynamics of the atomic and molecular systems—for example the molecular energy levels and the dispersion relationships for normal modes of molecular and lattice vibrations. Of particular interest is the study of diffusional processes in liquids and rubbers in the quasi-elastic scattering, which is inelastic scattering involving very small energy transfers. It is in fact a Doppler broadening process and from the broadening it is possible to obtain self-diffusion coefficients corresponding to the particular model used in the analysis.

Cold Neutrons

At room temperature the Maxwellian wavelength distribution of neutrons emerging from a reactor has a very low flux in the region of 5–10 Å, the wavelength range principally used in inelastic scattering studies². However, by inserting a small volume of liquid hydrogen (20 K) at the inner end of the neutron beam tube, the distribution is shifted to longer wavelengths to give considerable gain in flux at 5 Å.

Cold neutrons have wavelengths ~ 5 Å and their equivalent energy is 60 cal mol^{-1} ($\equiv 20 \text{ cm}^{-1} \equiv 0.025 \text{ eV}$). Thus their low energy makes them

ideal for the study of diffusional processes in which very small amounts of energy are transferred between the neutrons and the scattering molecule and also for studying molecular vibrational spectra by an anti-Stokes scattering process similar to the Raman effect in which the quanta of energy transferred to the neutrons are very much greater than the energy of the incident neutrons. For such quasi-elastic and inelastic experiments time-of-flight spectrometers² are most useful and these are available at AERE, Harwell, and at ILL, Grenoble.

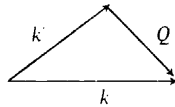
Energy and Momentum Transfer

If a neutron of incident wavelength λ and velocity V is scattered through an angle θ , in an inelastic process which changes the scattered wave-length to λ' and the velocity to V' , then the energy transfer is:

$$(\Delta E = \frac{1}{2}m(V'^2 - V^2) = \frac{\hbar^2}{2m}(k'^2 - k^2)$$

where m is the mass of the neutron and $k = 2\pi/\lambda$, $k' = 2\pi/\lambda'$ are the wave vectors.

The momentum transfer Q is shown in the vector diagram



and

$$\hbar Q = \hbar(k' - k)$$

For an inelastic process this is

$$Q^2 = 2 \left[\left(k^2 + \frac{m\Delta E}{\hbar^2} \right) - k \left(k^2 + \frac{2m\Delta E}{\hbar^2} \right)^{\frac{1}{2}} \cos \theta \right]$$

For small values of ΔE

$$Q \sim \frac{4\pi \sin(\theta/2)}{\lambda}$$

In a time-of-flight experiment the energy transfer is measured from the difference in velocity of the incident neutrons and neutrons scattered in a fixed direction. The momentum transfer is calculated from the incident wave-length, angle of scatter and ΔE . The time-of-flight spectrometer measures the quasi-elastic broadening and inelastic energy transfer spectrum at several well-defined angles of scatter simultaneously. This is a particularly important feature of diffusion studies because the diffusion constant is obtained from the energy broadening measured as a function of Q .

Coherent and Incoherent Neutron Scattering

Being uncharged, neutrons are scattered from the nuclei in the sample. The neutron has a magnetic moment characterized by a nuclear spin quantum

number $I = \frac{1}{2}$. Thus if a beam of neutrons is scattered from an array of identical nuclei with magnetic moments, the amplitude of the wave scattered at each nucleus varies according to the relative orientation of the spin states. Even in the case of an ordered array of nuclei the variation in amplitude of scatter from nucleus to nucleus of the same species gives rise³ to *incoherent scattering*; i.e. a process characterized by the absence of interference between waves scattered at different sites. There will also be a *coherent scattering* component of course.

The intensity of the coherent component of scatter is determined by mean square scattering lengths averaged over the whole assembly of nuclei, whereas the intensity of the incoherent part is determined by the mean of the square of the deviation from this average value.

The ratio of incoherent to coherent scattering intensities can be changed by altering the isotopic composition of the sample, e.g. replacing hydrogen by deuterium changes the scattering from primarily incoherent scattering to predominantly coherent scattering. Isotopes with zero nuclear spin, e.g. ^{12}C , ^{16}O , generate coherent scattering only. Coherent elastic scattering is used primarily in crystallography. Coherent inelastic scattering is used to determine dispersion relations of molecular and lattice vibrational modes. In this paper we are solely concerned with incoherent inelastic scattering which is used for motional quasi-elastic broadening studies and molecular spectroscopy.

Neutron Incoherent Inelastic Scattering by Polymers

A typical neutron incoherent inelastic time-of-flight spectrum⁴ of a polymer is shown in *Figure 1*. This spectrum of a 0.002 inch film of poly(propylene

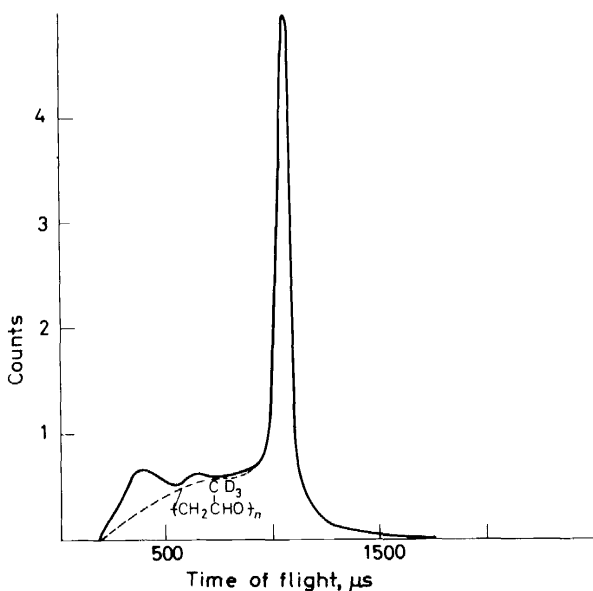


Figure 1. Time-of-flight spectrum of poly(propylene oxide).

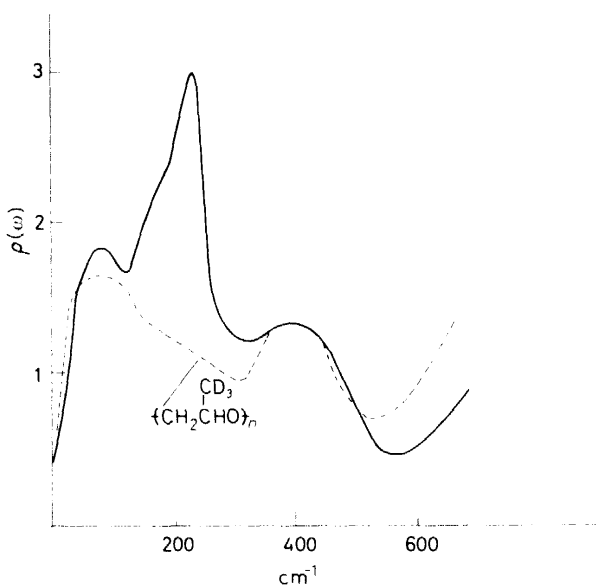


Figure 2. $\rho(\omega)$ for poly(propylene oxide) — and poly(trideuteriopropylene oxide) - - - - -.

oxide) has two major features, an elastic (or quasi-elastic) peak for neutrons scattered with virtually unchanged energy and an inelastic peak in which the neutrons have acquired a quantum of energy from the polymer molecules. Conversion of the inelastic part of this spectrum into a 'wave-number-shift from the elastic peak' spectrum in *Figure 2* shows that the inelastic peak is a vibrational band centred at 228 cm^{-1} .

If we now consider the scattering cross-sections of the nuclei for cold neutrons:

Scattering cross-sections (barns)		
	σ_{coh}	σ_{incoh}
^{12}C	5.6	0
^{16}O	4.2	0
^1H	1.8	79.7
^2D	7.6	2.0

then the incoherent scatter is dominated by scattering from protons in the sample. Further the intensity of a vibrational band is proportional to

- (a) the number of protons involved in the normal modes, and
- (b) their mean square amplitude of displacement in the mode.

Thus the band at 228 cm^{-1} is tentatively assigned as the $-\text{CH}_3$ group fundamental torsional vibration. This is confirmed by studying $-\text{[CH}(\text{CD}_3)\text{CH}_2\text{O]}_n-$ since the Table shows that this isotopic substitution should greatly diminish the intensity of the torsional vibration. In fact *Figure 2* shows that the band disappears.

Neutron incoherent inelastic scattering is a useful tool in molecular spectroscopy because *all* vibrational modes are active; the usual optical selection rules do not apply. Also, of course, selective deuteration is a powerful aid to assignment. However, the main preoccupation of this paper is concerned with the quasi-elastic peak.

Motional Studies of Rubbers by Quasi-elastic Incoherent Neutron Scattering

In neutron incoherent inelastic scattering experiments from simple liquids the elastic peak is broadened by exchange of energy between the neutrons and what is effectively a continuum of classical low-energy modes of motion available to the molecules in the liquid. In effect the neutrons undergo a Doppler shift in their velocities and hence the phenomenon is known as 'Doppler broadening' of the quasi-elastic peak. The broadening increases with increasing momentum transfer and is usually proportion to Q^2 .

Theoretically the interpretation of the broadening assumes that, in the liquid, the molecule reorientates faster than it translates and then the broadening function of the elastic peak can be obtained from a model of simple diffusion (governed by Fick's law for macroscopic diffusion). It is convenient to define a scattering law $\tilde{S}(Q, \varepsilon)$ which is even in energy gain and loss and this is related to the function $\check{S}(Q, \varepsilon)$ obtained by experiment by:

$$S(Q, \varepsilon) = \exp(-\varepsilon/2kT) \check{S}(Q, \varepsilon)$$

Theories of quasi-elastic scattering give $\tilde{S}(Q, \varepsilon)$ and for the simple diffusion model mentioned above

$$\tilde{S}(Q, \varepsilon) = \frac{\pi \hbar D Q^2}{(\hbar D Q^2)^2 + \varepsilon^2}$$

Thus the broadening function of the elastic peak is a Lorentzian of half-width

$$\Delta\varepsilon_{\frac{1}{2}} = 2\hbar D Q^2$$

In practice the Lorentzian will be convoluted with the Gaussian form of the elastic peak and the overall quasi-elastic should be a Voigt function. For simple liquids this is generally found to hold⁵.

As yet there is no theoretical scattering law for segmental diffusion of a polymer which may be calculated and compared with an observed neutron scattering spectrum. Calculations for an isolated chain whose motion takes place without hindrance indicate that a Lorentzian scattering law would be found at the limit of high Q values⁶. However, it is necessary to extract some simple and objective parameter from the data if different samples under different conditions are to be compared. Since the observed scattering law for poly(dimethylsiloxane) can be closely approximated by a Lorentzian we have continued to measure half widths and find that they can be related to the momentum transfer Q by the expression

$$\Delta\varepsilon_{\frac{1}{2}} = 2\hbar D_{\text{eff}} Q^2$$

At the present time this effective diffusion coefficient appears to be the best parameter to extract from the data.

The fit of our experimental results to Voigt functions are similar to those

of Figure 2 (broken curve) in reference ⁶. The poorness of fit in the wings of the functions is probably caused by the need for additional Lorentzian terms⁷ to describe more completely the segmental motion.

In this connection it should be noted that theories of polymer diffusion which include hydrodynamic interactions show that the Q dependence of the diffusion broadening in the limit of low Q values may involve higher powers, e.g. Q^3 or Q^4 ⁷. With the resolutions and in the temperature ranges now available such deviations are not serious although there are indications that at high resolution, high temperature experiments may reveal a non-linear dependence of the $S(Q, \omega)$ half-width on Q^2 for poly(dimethylsiloxane).

In practice, as we have noted above, the symmetrical form of the scattering law is obtained convoluted with the Gaussian resolution function of the spectrometer; tables and comparisons with calculated convolutions were used⁵ to determine the Lorentzian contributions to the Voigt functions.

In Table 1 are recorded effective diffusion coefficients (D_{eff}) at 20 °C, activation parameters and pre-exponential factors for the polymers examined. The temperature dependence of the diffusion coefficients have been expressed by a simple Arrhenius law $D_{\text{eff}} = D_0 \exp[-\Delta E/RT]$. In Figure 3, a plot of some deconvoluted half-widths versus Q^2 for poly(trideuteriopropylene oxide) gives an idea of the accuracy of the derivation of values of D_{eff} .

Table 1. Effective diffusion coefficients and their temperature dependences

	D_{eff} at 20 °C $\times 10^5 \text{ cm}^2 \text{ s}^{-1}$ (* indicates extrapolated values)	$D_0 \times 10^3 \text{ cm}^2 \text{ s}^{-1}$ (From $D = D_0 \exp[-\Delta E/RT]$)	$\Delta E \text{ kJ mol}^{-1}$
$\begin{array}{c} \text{CH}_3 \\ \\ \text{---Si---O---} \\ \\ \text{CH}_3 \end{array}$	2.09	0.5 ± 0.2	7.5
$\begin{array}{c} \text{CH}_3 \\ \\ \text{---Si---O---} \\ \\ \text{C}_6\text{H}_5 \end{array}$	0.62	0.65 ± 0.25	11.4
$\begin{array}{c} \text{CH}_3 \\ \\ \text{---C---CH}_2\text{---} \\ \\ \text{CH}_3 \end{array}$	0.04*	4.5 ± 2.5	22.0
$\left. \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{---CH---CH}_2\text{---O} \\ \\ \text{CD}_3 \\ \text{---CH---CH}_2\text{---O} \\ \\ \text{CH}_3 \\ \text{---CD---CD}_2\text{---O} \end{array} \right\}$	0.27*	7.0 ± 3.0	19.0
$\text{---CH}_2\text{---CH}_2\text{---O}$	0.20*	20.0 ± 10.0	22.0

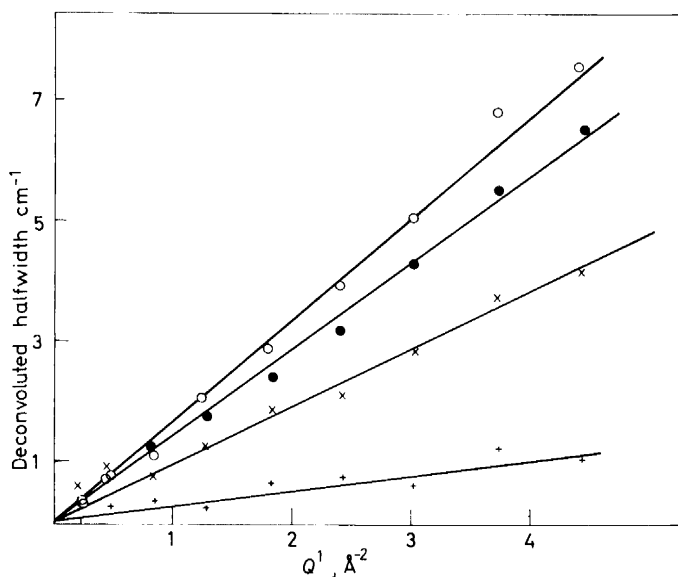


Figure 3. Q dependence of deconvoluted half-width for poly(trideutrioxypropylene oxide) at \circ 119, \bullet 104, \times 71 and $+$ 22°C.

The Origin of Doppler Broadening

In our earliest experiments we measured D_{eff} at constant temperature as a function of degree of polymerization for a series of dimethylsiloxane oligomers and polymers. Figure 4 shows that as the degree of polymerization increases D_{eff} decreases to a limiting value of $2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. If the poly-(dimethylsiloxane) is frozen to a glass the broadening disappears, and we

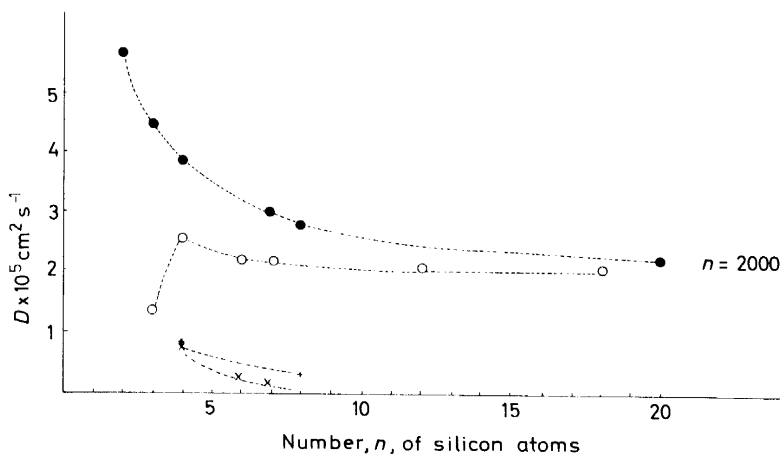


Figure 4. ' D_{eff} ' as a function of chain length for poly(dimethylsiloxane).

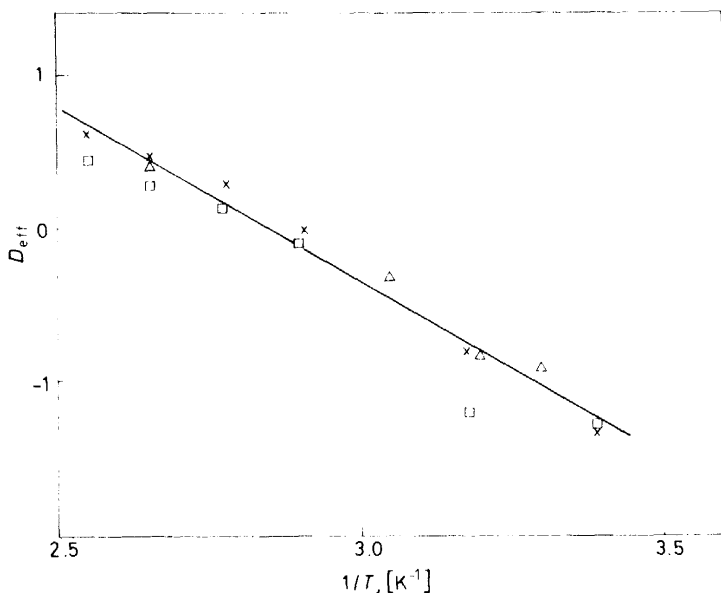
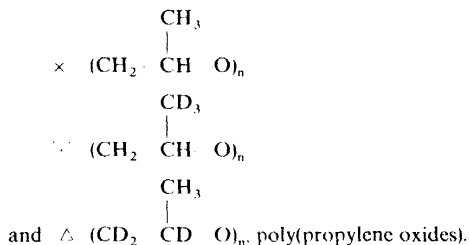


Figure 5. Temperature dependence of D_{eff} for



conclude that the motional broadening is characteristic of motion in the rubbery state.

The effective diffusion coefficients calculated from the Doppler broadening of the quasi-elastic peaks of the selectively deuterated poly(propylene oxides) are all plotted in *Figure 5* as a function of reciprocal absolute temperature. Within experimental error all these data can be represented by the same equation:

$$D = 7.2 \times 10^{-3} \exp[-2300/T] \text{ cm}^2 \text{ s}^{-1}$$

These results, taken together with the fact that D_{eff} decreases to a finite limiting value as chain length increases, confirm that the Doppler broadening arises primarily from the chain-link motion of the backbone of the polymer molecule⁵ and that the motion of the side groups contributes very little to the observed broadening. At high temperatures, where the measurements are most precise, the diffusion coefficients calculated for $\text{---[CH}_2\text{---CH(CD}_3\text{)O]}_n\text{---}$

are systematically very slightly lower than for the protonated material. However the differences are too small to affect our overall conclusion.

We have now observed the broadening in five high molecular weight polymers in the raw rubber state and have confirmed that low degrees of cross-linking at a level normally encountered in elastomers do not noticeably change the broadening or the magnitude of the diffusion coefficients obtained therefrom.

In all five materials the broadening is a linear function of Q^2 in the ranges of Q and temperature studied and with resolution currently available. Again this is consistent with identification of segmental diffusion as a translational phenomenon. The possibility of a significant contribution from rotational diffusion of the methyl side groups about the H_3C -main chain bond can be discounted.

Temperature Coefficients of Doppler Broadening

The coefficients obtained from the momentum transfer dependence of the Doppler broadening fall exponentially with decrease in temperature for each rubber studied. The results are summarized in *Figure 6*. Good Arrhenius

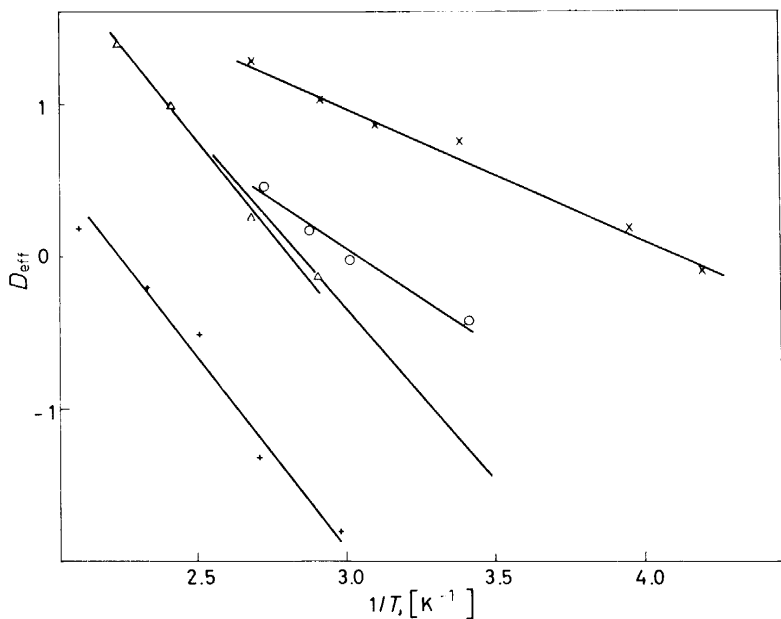


Figure 6. Temperature dependence of D_{eff} for. \times , poly(dimethylsiloxane), \circ , poly(methylphenylsiloxane), $+$, poly(isobutene), $-$, poly(propylene oxide) and Δ , poly(ethylene oxide).

plots are obtained in each case and simple activation energies can be obtained. This is in marked contrast to the $\log(\text{frequency})/\text{temperature}$ plots obtained from nuclear spin-lattice relaxation and dielectric measurements in rubbers. Over comparable temperature ranges, i.e. up to 100°C above the

glass transition temperature of the polymer, the relaxation methods sometimes give plots which are linear in $(T - T_g)^{-1}$ rather than T^{-1} .

Thus it is believed that quasi-elastic neutron scattering measurements provide a method of studying the internal rotational wriggling motions of polymer chains in the rubbery state and also in solution. An adequate model for interpreting the results has still to be developed and the precise form of the experimental scattering law as a function of momentum transfer has still to be established. Poly(dimethylsiloxane) will be a useful material for these experiments and the high flux beam reactor in the Institute Laue-Langevin in Grenoble should provide a major new facility for advancing our knowledge in this field.

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