

**NEUTRON TRANSMISSION STUDY OF THE ROTACIONAL FREEDOM  
OF METHYL GROUPS IN POLYDIMETHYLSILOXANE**

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# NEUTRON TRANSMISSION STUDY OF THE ROTACIONAL FREEDOM OF METHYL GROUPS IN POLYDIMETHYLSILOXANE

L. Q. Amaral, L. A. Vinhas and S. B. Herdades,\*

## ABSTRACT

The total neutron cross section of polydimethylsiloxane has been measured as a function of neutron wavelength in the range  $4\text{\AA}$  to  $10\text{\AA}$  at room temperature, using a slow neutron chopper and time of flight spectrometer. Scattering cross sections per hydrogen atom were obtained and the slope ( $12.2 \pm 0.2$  barns/ $\text{\AA}$ ) has been derived.

Comparison with calculated neutron cross sections using the Krieger Neikin formalism for different dynamical situations as well as comparison with calibration curves relating the slope to the barrier hindering internal rotation indicates the existence of practically free rotation of  $\text{CH}_3$  groups about their  $\text{C}_3$  axis.

## 1. Introduction

The application fields of neutron scattering techniques have been broadened into various branches of science and technology by unconventional uses of these techniques. In the past few years there has been a remarkable extension into several branches of chemistry<sup>(3,7)</sup>, including the study of polymers.

The synthetic organic compounds, where oxygen acts as a bridge between two silicon atoms, are usually called silicones, and there is today a separate organosilicon chemistry somewhat analogous to that of carbon. The silicone polymers, in fluid or rubber form depending on the degree of polymerization and cross-linking, find a wide variety of applications and are of great technological interest. The special properties of silicones when compared to hydrocarbon polymers are<sup>(20) (23)</sup>:

- 1) thermal and oxidative stability at high temperatures ( $250^\circ\text{C}$ )
- 2) flexibility and elasticity at very low temperatures ( $-100^\circ\text{C}$ )
- 3) relatively little change in viscosity with changes in temperature or with rate of shear
- 4) high compressibilities
- 5) chemical and physical inertness; they are not compatible with organic materials and are water repellant
- 6) unusual surface properties and good electrical insulation.

Most of the physical properties of the silicones can be related in a fairly straightforward way to the molecular structure and have been attributed to chain flexibility and to very low intermolecular cohesive forces, due to molecular rotations.

The most common silicone fluid is polydimethylsiloxane (PDMS),  $\text{CH}_3(\text{CH}_3)_2\text{SiO} \left[ \text{Si}(\text{CH}_3)_2 \right]_{n-1} \text{Si}(\text{CH}_3)_3$ , with viscosities varying from 0.65 cst to over  $10^6$  cst depending on the value of  $n$ . The crystal structure, the chain conformations and related low frequency molecular motions in PDMS have been investigated by a variety of techniques<sup>(12)</sup>. The melting transition occurs at about  $-55^\circ\text{C}$ , but low temperature properties are present until

the second order transition point in the region of  $-120^{\circ}\text{C}$ .

The existence of almost free rotation of  $\text{CH}_3$  groups about siloxy bonds in PDMS has been suggested from diffraction studies<sup>(26,27)</sup>. NMR studies of several methyl silicones<sup>(13,14,15,19,21,24)</sup> have indicated that, besides the  $\text{Si}(\text{CH}_3)_2$  group rotation about the siloxy bond, an almost free rotation of  $\text{CH}_3$  groups about their  $\text{C}_3$  symmetry axes (C-Si bond) occurs, as well as some form of translational motion. There is no indication that the  $\text{CH}_3$  rotation be sensible to the degree of polymerization, being due essentially to intramolecular forces

It is accepted<sup>(20)</sup> that methyl rotation, that persists at low temperatures and is still extensive at  $-196^{\circ}\text{C}$ <sup>(24)</sup>, leads to occupation of additional volume, what increases the distance between adjacent molecules. Thus the intermolecular forces are markedly lower than in hydrocarbons, what would explain the unique physical properties of the methyl silicones. The whole  $(\text{CH}_3)_2\text{Si}$  group moves also easily about the Si-O bond; because of this, the silicone chains are able to coil and uncoil rather freely.

The NMR results evidence reorientation of  $\text{CH}_3$  about their  $\text{C}_3$  axes, and indicate an almost free rotation. However, due to the interaction time of a NMR experiment ( $\sim 10^{-9}$  sec), a hindered rotation with a small barrier may appear as free rotation. Slow neutrons have a much shorter interaction time ( $\sim 10^{-11}$  sec) and are specially valuable for studying  $\text{CH}_3$  rotations, because of the high hydrogen scattering cross section and the large amplitude of motion of the protons<sup>(4)</sup>. In the case of hindered rotation, the  $\text{CH}_3$  torsional fundamental frequency is easily seen in inelastic neutron scattering spectroscopy, while it is very weak and difficult to detect in infra-red and Raman spectra

Two studies on neutron inelastic scattering by PDMS have been published: one by Henry and Safford<sup>(12)</sup>, that studies also the effects of cross linking and fillers, and analyses the results in terms of free  $\text{CH}_3$  group rotation and another by Allen<sup>(2)</sup>, that arrives to a barrier of  $\sim 2$  kcal/mol hindering the methyl rotation. The main difference is in the interpretation of the observed inelastic peak, that the first attributes to an envelop of free rotational levels, with peak position given by the effective rotational mass in the Krieger-Nelkin (KN) formalism<sup>(18)</sup>, while the second attributes it to the first torsional level of a hindered rotational barrier.

This contradictory explanation can be cleared out by studying the total neutron cross section as a function of neutron wavelength, which is a more limited technique, but can prove valuable in clarifying this doubt<sup>(4) (9)</sup>.

This paper presents slow neutron transmission measurements of PDMS in the neutron wavelength interval  $4\text{\AA}$  to  $10\text{\AA}$ , from which the total incoherent scattering cross section per proton,  $\sigma_H$ , has been derived. Results are analysed in terms of rotational freedom of hydrogenous molecular groups.

## 2. Neutron Scattering and Rotational Freedom

The neutron scattered spectrum from a system undergoing free rotation consists of a broad inelastic distribution without an elastic component. With increasing hindrance, the broad, free rotational component would evolve to a sharper maximum at the torsional frequency and

there would be a corresponding elastic peak

In the case of freely rotating molecules, the KN formalism<sup>(18)</sup> may be applied for calculating the neutron scattering cross-sections, provided  $A \ll E_n < E_{vib}$ , where  $E_n$  is the neutron energy,  $A$  is the rotational constant and  $E_{vib}$  is the vibrational threshold energy. The shape and the position of the maximum of the KN spectra depends on temperature, scattering angle and two parameters: an effective vibrational frequency  $\bar{\omega}$  and an effective proton mass for rotation and translation  $M_p$ , that depends on the molecular shape of the rotating group and the number of degrees of rotational freedom.

The approximations involved in the KN theory make questionable its application to the condensed state, and in general no agreement with differential scattering cross section is obtained even in the case of freely rotating molecules<sup>(17)</sup>. All data appear to be shifted to higher energies than calculated from theory, what means that a lower effective mass is always necessary to give agreement with data. It has been found<sup>(17)</sup> that experimental data lie between the calculated KN spectra and a Boltzman distribution of an uniformly dense set of energy states of the scattering system, which would be expected to give an upper limit to the energy distribution of the scattered neutrons.

These results show that it can be misleading to rely on agreement of KN theory with inelastic spectra as an indicator of the effective rotational mass in free rotation. It is more justified to compare the spectra of the investigated compound with spectra of standard substances and analyse the broadening of the inelastic peak, which is inversely related to the hindrance<sup>(17)</sup>. However, there is not yet an empirical correlation between broadening and barrier height nor does a suitable theoretical frame work exist for calculating this relation.

On the other hand, total neutron scattering cross section, being an integral quantity, can be better explained in terms of KN formalism<sup>(6)</sup>. The results show clearly that the total cross-section of a variety of molecules in gaseous form can be described by the KN model; in the liquid and solid states, an agreement with the KN calculation may be considered as a verification of the freedom of molecular rotations.

In hydrogenous compounds, where neutron scattering is essentially incoherent and due to the H atom, neutron transmission measurements provide the total incoherent cross section per proton,  $\sigma_H$ . The curve of  $\sigma_H$  as a function of neutron wavelength  $\lambda$  can be approximated by a straight line, in the region of "cold neutrons" (with energy  $\ll 0.025$  eV). The slope of this line is determined by the inelastic scattering, in which the neutron gains energy from molecules in populated excited states. At room temperature, the main contribution to the inelastic scattering is due to de-excitation of energy levels corresponding to torsional or free rotational motions of the molecules or molecular groups containing hydrogen<sup>(6)</sup>.

In the case of free rotation of molecules or molecular groups, the KN formalism may be applied for calculating  $\sigma_H$ . The slope of the cross section curve is given essentially by the proton effective mass  $M_p$  and the effective vibrational parameter  $\bar{\omega}$  has the effect of translating the curve. The slope decreases with increasing  $M_p$  and  $\sigma_H$  increases with increasing  $\bar{\omega}$ . Details of the KN theory are given in Appendix A.

Furthermore, for a given moment of inertia for rotation, the slope of  $\sigma_H \times \lambda$  increases with

the freedom of motion of the H atoms<sup>(7)</sup>; this slope has been empirically correlated with the barrier hindering the internal rotation of the molecular groups  $\text{NH}_4$  and  $\text{CH}_3$ . There are two calibration curves relating the slope with the barrier for internal rotation: one obtained by Rush for  $\text{NH}_4$  from the study of ammonium salts<sup>(29-34)</sup> and another obtained by Herdade<sup>(10)</sup> for  $\text{CH}_3$  in non-associated liquids. The curve obtained for  $\text{NH}_4$  has also been used for  $\text{CH}_3$ , since the rotational masses of both groups are close and the slope is the same for both groups when freely rotating in the gas state. The difference between the two curves for small barriers, close to the limit of free rotation ( $< 0.4$  kcal/mol) is certainly due to the gas limit used by Rush. For barriers larger than 1 kcal/mol, Herdade's curve gives results larger than the ones from Rush by  $\sim 1$  kcal/mol, what is probably due to a contribution from the molecular movements in the liquid state, since the barrier for hexamethylbenzene in the solid state agrees with Rush's curve<sup>(35)</sup>. Barriers of the order of some tenths of kcal/mol up to 10 kcal/mol may be detected through these calibration curves.

It is worthwhile observing<sup>(6)</sup> that in the study of ammonium salts broad inelastic distributions were obtained for compounds having total cross sections with large slopes, what was interpreted as arising from free rotation of the  $\text{NH}_4$  group.

Thus the freedom of rotational motion in PDMS can be discussed by comparing  $\sigma_{\text{H}}$  with KN calculations and with the existing calibration curves.

### 3. Experimental

The total neutron cross section of PDMS as a function of neutron wavelength  $\lambda$  in the range 4 to 10 Å (5 meV to 0.8 meV) has been measured using a slow neutron chopper and time-of-flight spectrometer<sup>(3) (11)</sup> at the IEA-R1 swimming pool research reactor. A Pb(111) filter 9 cm thick was used to reduce thermal neutrons from the direct beam. The flight path was 1.5 m, and the chopper operated at 5000 and 5700 rpm to cover the  $\lambda$  interval of interest. The wavelength resolution varied from 0.1 Å at  $\lambda = 1$  Å to 0.3 Å at  $\lambda = 10$  Å.

To minimize the effect of possible drifts in the neutron beam, the data for the transmission and background measurements were taken in short cycles, besides being controlled by a beam monitor.

The sample used was Union Carbide silicone fluid L-45, with a viscosity of 100 centistokes and density 0.962 g/cm<sup>3</sup> at 25°C. The average molecular mass of PDMS can be calculated from (22):

$$\log \eta (\text{cstks at } 25^\circ\text{C}) = 1.00 + 0.0123 M^{0.5}$$

For this sample  $M \cong 6.600$ ; considering that  $M = 74n + 14$  this means  $n = 89$  in the structure formula for the polymer

Data were taken at room temperature (23.5°C), with the sample in an aluminium holder with internal spacing 0.256 cm. The sample thickness  $t$  was chosen to give a transmission  $T$  in the interval  $1/e$  to  $1/e^2$ <sup>(25)</sup>, for better precision in the determination of the total cross section<sup>(16)</sup>  $\sigma = \ln(T^{-1})/tN$ , where  $N$  is the number of molecules/cm<sup>3</sup>. To obtain the average scattering cross section per hydrogen atom,  $\sigma_{\text{H}}$ , the total cross-section was corrected for total neutron absorption and for scattering by Si, C and O atoms. Time-of-flight data processing and

cross section computation have been carried out by means of the code TVSC<sup>(11)</sup>.

#### 4 Results and Discussion

Appendix B gives the measured neutron cross-sections and figure 1 shows the obtained values of  $\sigma_H$  of PDMS as function of neutron wavelength. The slope  $b_s = (12.2 \pm 0.2) \text{b}/\text{\AA}$  of the experimental curve was determined by a weighted least square fit to the data in the wavelength range 5 to 10 \AA; the linearity of the experimental results over this range is very good.

Following Safford's interpretation<sup>(12)</sup>, the hindrance for  $\text{CH}_3$  rotation in PDMS appears only at  $-123^\circ\text{C}$ , and room temperature spectra cannot be even approximately accounted for only by free rotation about the threefold symmetry axis of the  $\text{CH}_3$  groups; it would be necessary to assume also free rotation of the center of mass of the  $\text{CH}_3$  group in a plane as well as translation with large amplitudes, because agreement of KN curve with data is obtained for  $M_e \sim 2 - 5$ , while  $M_e \sim 9$  assuming only free threefold rotation. However, according to the preceding section, it is not reliable to deduce dynamical situations from the effective mass that brings agreement between KN calculation and inelastic spectra.

Here the KN formalism was applied in the calculation of  $\sigma_H$ , for  $(\text{CH}_3)_2\text{Si}$  groups forming hypothetical siloxane chains, with the effective mass  $M_e$  and the effective frequency  $\bar{\omega}$  as adjustable parameters.

The effective proton masses have been calculated by the Sachs-Teller mass tensor concept<sup>(18)</sup> in three different dynamical situations, assuming the translational mass to be infinite:

- a) rotation of the  $(\text{CH}_3)_2\text{Si}$  group about an axis passing through the Si atom and perpendicular to the Si-C bond.
- b) rotation of  $\text{CH}_3$  group about their  $\text{C}_3$  axis
- c) simultaneous rotation of  $(\text{CH}_3)_2\text{Si}$  and  $\text{CH}_3$  groups.

The value  $180^\circ$  is ascribed to the angle C-Si-C, instead of the tetrahedral value  $110^\circ$ . The following atomic distances were used<sup>(1) (24)</sup>: H-H = 1.79 \AA, C-H = 1.094 \AA, C-Si = 1.92 \AA. Calculations give  $M_e \sim 64$  for case a,  $M_e = 9$  for case b and  $M_e \sim 8$  for case c. Further rotational degrees of freedom for the center of mass of the  $\text{CH}_3$  groups uncoupled could reduce  $M_e$  to 6 and translation could bring  $M_e$  down to  $\sim 4$ .

KN calculations of  $\sigma_H$  have been performed for several values of  $M_e$  in the range 3 - 64 uam and for  $\bar{\omega}$  in the range 0.1 - 0.36 eV, considering the frequency vibrations<sup>(5)</sup> of  $\text{CH}_3$  and  $(\text{CH}_3)_2\text{Si}$ .

Figure 1 shows the calculated KN curves for  $M_e = 9$  uam,  $\bar{\omega} = 0.1$  eV and for  $M_e = 64, 9, 8, 7, 5$  uam,  $\bar{\omega} = 0.3$  eV. As  $\omega$  and  $M_e$  affect the KN curve in different ways, the determination of the two parameters is almost independent. The effective vibration that brings agreement with calculation is  $\omega = 0.3$  eV, a value between the  $\text{CH}_3$  stretching vibration ( $2900 \text{ cm}^{-1}$ ) and deformations ( $\sim 1450 \text{ cm}^{-1}$ )<sup>(5)</sup>.

The value  $M_e = 8$  gives the best agreement between experimental data and KN



calculation, but considering only the slope of the curve an effective rotational mass of 8–9 would be enough for a reasonable agreement.

Table 1 and figure 2 show the correlation between  $M_e$  and the slope  $b_s$  obtained from the KN curves in the range 6 to 10Å.

TABLE I

$M_e$ (uam)	$b_s$ (b/Å)	$M_e$ (uam)	$b_s$ (b/Å)
64	3.1	9	11.8
50	3.8	8	12.4
40	4.6	7	12.8
30	5.8	6	13.6
20	7.7	5	14.1
15	9.3	4	14.7
10	11.4	3	15.1

Surely a free rotation of  $(CH_3)_2Si$  about the Si–O bond alone cannot explain the observed  $\sigma_H$ . The existence of practically free rotation of  $CH_3$  groups about their  $C_3$  axes in PDMS is necessary for the agreement between KN calculated curve and the experimental  $\sigma_H$ . However, the agreement of differential data with a very low effective mass, of 2 to 5,<sup>(12)</sup> has no physical meaning. There is indication that free rotation of  $(CH_3)_2Si$  about the Si–O bond also occurs, but neutron scattering is not very sensitive to large masses rotation, neither KN theory is so reliable that one can distinguish between  $M_e = 8$  and 9.

The main criticism about KN theory lies in neglecting low energy modes that could contribute to inelastic scattering, especially in liquid phase at room temperature. However, for PDMS the inelastic spectrum<sup>(12)</sup> shows that the  $CH_3$  contribution is dominant and we shall not be in large error by analysing  $\sigma_H$  as given essentially by  $CH_3$  movements. Within this approximation, the experimental slope can be used to measure the freedom of  $CH_3$  groups in PDMS.

The experimental slope  $b_s = (12.2 \pm 0.2)b/\text{Å}$  here reported is very close to the value 12.0  $b/\text{Å}$  previously obtained for liquid  $CH_3C \equiv CCH_3$  and solid  $(CH_3)_3SnF_2$ <sup>(29–34)</sup> at room temperature, in which free rotation of  $CH_3$  was assumed. Comparing this experimental result with the calibration curves for  $CH_3$ <sup>(10)</sup><sup>(29–34)</sup>, it is possible to derive an upper limit of 0.4 kcal/mol for the barrier hindering the methyl rotation in PDMS. However, a correction for other contributions than  $CH_3$  rotation to  $\sigma_H$  could increase this value.

Following Allen's interpretation<sup>(2)</sup>, the inelastic peak would be due to the  $1 \rightarrow 0$  torsional transition of a potential barrier of  $\sim 2$ kcal/mol. According to the calibration curves for the solid and liquid state, this barrier would allow for a slope of  $8-9$   $b/\text{Å}$ , a too low result when compared with the experimentally obtained  $b_s$ . It is very improbable that the rest of  $\sigma_H$  could be accounted for by other contributions due to low-frequency vibrations and further

degrees of freedom involving larger rotational masses.

The results for  $(\text{CH}_3)_2\text{SiCl}_2$ , used in the preparation of silicone polymers, gave a slope of  $(12.3 \pm 0.5)b/\text{\AA}^{(10)}$ , very close to the value here reported. This also corroborates the rather free rotation of  $\text{CH}_3$  in PDMS

## 5. Conclusion

Slow neutron transmission measurements indicate the existence of practically free rotation of methyl groups in polydimethylsiloxane. Considering that  $\sigma_H$  is given essentially by  $\text{CH}_3$  rotation, the obtained slope gives a value of 0.4 kcal/mol as an upper limit for the barrier hindering this rotation.

These results favour Safford's interpretation of neutron inelastic spectra in terms of free  $\text{CH}_3$  rotation, but show also that the very small effective mass necessary to bring agreement between KN calculations and inelastic spectra does not have a physical meaning and shall not be considered as an indication of the existence of further degrees of freedom, both rotational and translational, of the  $\text{CH}_3$  center of mass. Only simultaneous rotation of the whole  $(\text{CH}_3)_2\text{Si}$  group about the Si-O bond is compatible with neutron transmission data.

The unusual freedom of  $\text{CH}_3$  rotation about their  $\text{C}_3$  axes may be ascribed to the greater radius of the silicon atom (1.173Å) when compared with that from carbon (0.771Å), what makes the Si-C bond longer than the C-C bond. Furthermore, the relatively wide separation of the methyl groups, due to the presence of oxygen atom along the chain skeleton, tends to reduce the steric hindrance to this rotation.

## ACKNOWLEDGMENTS

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## FIGURE CAPTIONS

Fig. 1 - Scattering cross sections per hydrogen atom,  $\sigma_H$ , as a function of neutron wavelength  $\lambda$ . Experimental points and calculated KN curves.

- a -  $M_e = 9$ ,  $\bar{\omega} = 0.1 \text{ eV}$
- b -  $M_e = 9$ ,  $\bar{\omega} = 0.3 \text{ eV}$
- c -  $M_e = 64$ ,  $\bar{\omega} = 0.3 \text{ eV}$
- d -  $M_e = 8$ ,  $\bar{\omega} = 0.3 \text{ eV}$
- e -  $M_e = 7$ ,  $\bar{\omega} = 0.3 \text{ eV}$
- f -  $M_e = 5$ ,  $\bar{\omega} = 0.3 \text{ eV}$

Fig. 2 - Correlation between the effective proton mass  $M_e$  and the slope  $b_s$  obtained from the KN curves in the wavelength range 6Å to 10Å.

## APPENDIX A

## Krieger Nelkin Cross Section Calculation

## 1 Krieger Nelkin (KN) Formalism

In the Krieger-Nelkin (KN) formalism<sup>(18)</sup>, the operator formalism in slow-neutron scattering theory introduced by Zemach and Glauber<sup>(38) (39)</sup> is considered in an approximation in which molecular rotational and vibrational effects are explicitly separated. The combined effects of rotation and translation are treated in terms of the Sachs-Teller "mass tensor" concept<sup>(35)</sup>, which is derived on the basis of a rigid molecule Hamiltonian and extended to include interference effects. Only elastic vibrational transitions from the ground vibrational state are considered. The applicable neutron energy range is restricted to values large compared to the rotational level separation but below the vibrational threshold.

The methods applicable to the calculation of differential as well as total scattering cross sections and to molecules of arbitrary structure. Expressions in closed form for these cross sections are obtained through use of an approximate procedure for averaging over molecular orientations. In the case of hydrogenous molecules, the scattering by a given nucleus is described in terms of two parameters, an effective nuclear mass for rotation and translation, and a vibrational constant.

The total scattering cross section per proton is given by<sup>(28)</sup>:

$$\sigma_s(E_0) = \frac{\sigma_0}{2m\gamma E_0} \left[ \operatorname{erf} \left[ C^{1/2} \right] - (1-P)^{1/2} \exp(-CP) \operatorname{erf} \left[ C^{1/2}(1-P)^{1/2} \right] \right]$$

where

$$\operatorname{erf} Z \equiv \frac{2}{\sqrt{\pi}} \int_0^Z \exp(-t^2) dt$$

$E_0$  = neutron energy

$\sigma_0$  = free proton cross section (20.36 barns)

$m$  = proton mass

$\gamma$  =  $\frac{1}{4m\bar{\omega}}$  = mean-square vibrational amplitude of the proton

$\bar{\omega}$  = effective vibrational frequency (eV)

$C$  =  $M_{rt} E_0 / MT$

$P$  =  $\frac{8\gamma\nu^2 T}{M_{rt} + 8\gamma\nu^2 T}$  and  $\nu = \frac{m M_{rt}}{m + M_{rt}}$

$M_{rt}$  = effective proton mass.

For the calculation of  $\sigma_s(E_0)$  the code KR!GER (Fr68) has been elaborated in FORTRAN II-D.

## 2. Effective Proton Mass

The effective rotational-translational mass  $M_{rt}$  is given by

$$M_{rt} = \left[ \frac{1}{3} \text{spur} \left[ \eta^{-1} \right] \right]^{-1}$$

where

$\eta^{-1}$  is the Sachs-Teller mass tensor, given by

$$(\eta^{-1})_{ii} = \frac{r_i^2}{I_k} + \frac{r_j^2}{I_j} + \frac{1}{M}$$

$$(\eta^{-1})_{ij} = \frac{-r_i r_j}{I_k}$$

where

$r_i$  = coordinate of the bound H atom in the C.M. system

$I_i$  = moment of inertia around the  $i^{\text{th}}$  axis

$M$  = total molecular mass

The effective mass is thus given by the sum of the elements of the principal diagonal of the mass tensor

An equivalent way of calculating  $M_{rt}$  is through:

$$\frac{1}{M_{rt}} = \frac{1}{m_r} + \frac{1}{M}$$

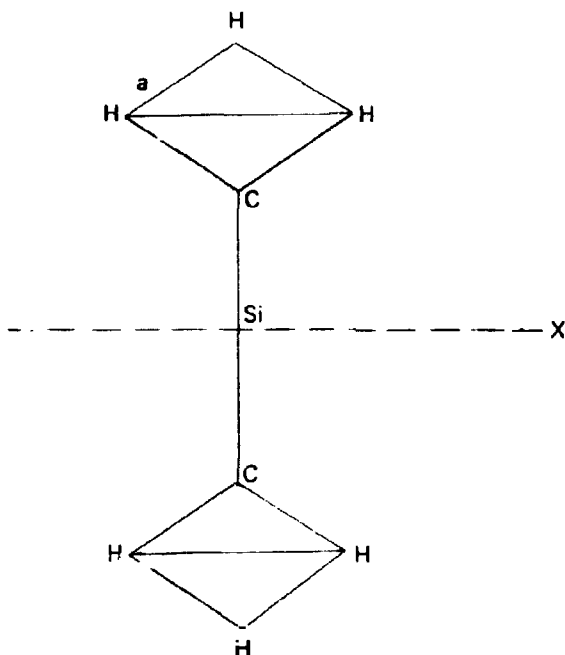
$$m_r = \frac{3}{d_x^2/I_x + d_y^2/I_y + d_z^2/I_z}$$

where

$d_i$  = distance from the bound H atom to the  $i^{\text{th}}$  principle axis of inertia of the molecule

$m_r$  = effective rotational mass

The approximate structure of PDMS, when the value  $180^\circ$  is ascribed to the angle C-Si-C, instead of the tetrahedral value  $110^\circ$ , is given by<sup>(1) (26)</sup>:



$$\begin{aligned}
 a &= \text{H-H} = 1.79 \text{ \AA} \\
 &\text{C-H} = 1.094 \text{ \AA} \\
 &\text{C-Si} = 1.92 \text{ \AA}
 \end{aligned}$$

In the calculation for methyl silicone the translational mass is assumed to be infinite, what is equivalent to consider only rotations.

In the case of  $\text{CH}_3$  rotation about the fixed  $\text{C}_3$  axis:

$$\begin{aligned}
 I_x &= I_y = \infty \\
 I_z &= m_{\text{H}} a^2 = 3.204 \text{ uam \AA}^2 \\
 m_r &= 9.0 \text{ uam}
 \end{aligned}$$

For rotation of the group  $(\text{CH}_3)_2\text{Si}$  about the Si-O bond:

$$\begin{aligned}
 I_y &= I_z = \infty \\
 I_x &= 122.84 \text{ uam \AA}^2 \\
 m_r &\sim 64 \text{ uam}
 \end{aligned}$$

For the two simultaneous rotations

$$\begin{aligned}
 I_x &= 122.84 \text{ uam \AA}^2 \\
 I_z &= 3.204 \text{ uam \AA}^2 \\
 I_y &= \infty \\
 m_r &\sim 8 \text{ uam}
 \end{aligned}$$

Further degrees of freedom, both rotational and translational, would decrease  $M_{\text{rx}}$ .

### 3. Effective Vibrational Frequency

The effective vibrational frequency  $\bar{\omega}$  may be calculated from the normal modes of vibration from<sup>(28)</sup>

$$\gamma = \frac{1}{4m\bar{\omega}} = \frac{1}{5} \sum_{\lambda} \left[ \frac{C^{\lambda}}{\omega^{\lambda}} \right]^2$$

where

$$\begin{aligned} C^{\lambda} &= \text{amplitude vector corresponding to the } \lambda^{\text{th}} \text{ mode} \\ \omega^{\lambda} &= \text{angular frequencies of the } \lambda \text{ mode} \end{aligned}$$

The use of this expression places an upper limit on the range of neutron energy to which the theory can be applied,  $E_n < E_{\text{vib}}$ , where  $E_{\text{vib}}$  is the lowest hydrogen vibrational frequency. It should also be noted that, within this limit, the vibrational parameter only affects the elastic scattering; therefore this parameter should not affect the slope of  $\sigma_s$ , due entirely to inelastic scattering.

For PDMS this parameter has not been calculated exactly.

### 4. Conditions for Validity

The KN is applicable only when  $A \ll E_n < E_{\text{vib}}$  where  $A$  is the rotational constant of the molecule,  $E_{\text{vib}}$  is the vibrational threshold energy and  $E_n$  is the neutron energy.

$$A = \frac{h}{8\pi^2 c I} \text{ cm}^{-1} = \frac{27994 \times 10^{-40}}{I} \text{ cm}^{-1}$$

When rotation of  $\text{CH}_3$  about the fixed  $\text{C}_3$  axis is assumed,

$$I = m_{\text{H}} a^2 = 5.34 \times 10^{-40} \text{ g cm}^2 \text{ and}$$

$$A = 0.647 \text{ meV.}$$

When rotation of the group  $(\text{CH}_3)_2\text{Si}$  about the Si-O bond (axis X) is assumed,

$$I_x = 206 \times 10^{-40} \text{ g cm}^2 \text{ and}$$

$$A \cong 0.0273 \text{ meV.}$$

For the neutron wavelength interval 4 to  $10\text{\AA}$  (5 meV to 0.8 meV) the condition of validity is fully satisfied for the second hypothesis, and approximately valid for the first case.

However it has been noted<sup>(28)</sup> that the KN approximation provides reasonable agreement with the experimental total cross section even at very low energies, although the method is supposed to break down as the neutron energy  $E_n$  approaches the rotational level spacing.

## APPENDIX B

## Neutron Cross Section Measurements of Polydimethylsiloxane

The measured sample transmission is given by

$$T = \frac{A - BA}{D - BD},$$

where

A and D are the intensity rates with the sample and without the sample in the neutron beam, and BA and BD are the correspondent background rates.

For PDMS,  $\text{Si}_n \text{O}_{n-1} \text{C}_{2n+2} \text{H}_{6n+6}$ , the proton scattering cross section is obtained from the transmission through

$$\sigma_H = \frac{\ln T^{-1} / Nt - K}{6n + 6}$$

where

N is the number of PDMS molecules/cm<sup>3</sup>, obtained from Avogadro's  $N_0$ , the sample density  $\rho$  and the molecular weight  $A = 74n + 14$

$$N = N_0 \rho / A$$

t is the sample thickness

K is the total absorption cross-section plus the scattering from the remaining atoms

$$K = n\sigma(\text{Si}) + (n-1)\sigma(\text{O}) + (2n+2)\sigma(\text{C}) + (6n+6)\sigma_a(\text{H})$$

For  $n = 89$  results

$$\sigma_H = 82\,201 \ln T^{-1} - (2.56 + 0.198 \lambda)$$

The table gives the values of  $\ln T^{-1}$  and  $\sigma_H$ , with their statistical errors, for neutron wavelengths  $\lambda$  in the interval 4Å to 10Å. For  $\lambda > 8\text{Å}$ , the values in the table are averages over two, three and four points, since the statistical errors increase as the intensity of the maxwellian neutron spectrum falls down.

TABLE II

$\lambda(\text{\AA})$	$\ln T^{-1}$	$\sigma_H$ (barns)
3.91	$1.019 \pm 0.004$	$80.4 \pm 0.3$
4.00	$1.039 \pm 0.004$	$82.1 \pm 0.3$
4.08	$1.051 \pm 0.005$	$83.0 \pm 0.4$
4.17	$1.053 \pm 0.005$	$83.2 \pm 0.4$
4.25	$1.062 \pm 0.005$	$83.9 \pm 0.4$
4.34	$1.075 \pm 0.005$	$85.0 \pm 0.4$
4.42	$1.087 \pm 0.005$	$85.9 \pm 0.4$
4.51	$1.097 \pm 0.005$	$86.7 \pm 0.4$
4.59	$1.125 \pm 0.006$	$89.0 \pm 0.5$
4.67	$1.128 \pm 0.006$	$89.2 \pm 0.5$
4.75	$1.136 \pm 0.006$	$89.9 \pm 0.5$
4.84	$1.138 \pm 0.006$	$90.0 \pm 0.5$
4.93	$1.158 \pm 0.006$	$91.6 \pm 0.5$
5.01	$1.174 \pm 0.006$	$93.0 \pm 0.5$
5.10	$1.173 \pm 0.007$	$92.9 \pm 0.6$
5.18	$1.199 \pm 0.007$	$95.0 \pm 0.6$
5.26	$1.204 \pm 0.003$	$95.4 \pm 0.2$
5.35	$1.218 \pm 0.003$	$96.5 \pm 0.2$
5.43	$1.223 \pm 0.003$	$96.9 \pm 0.2$
5.52	$1.243 \pm 0.003$	$98.5 \pm 0.2$
5.60	$1.254 \pm 0.003$	$99.4 \pm 0.2$
5.69	$1.271 \pm 0.003$	$100.8 \pm 0.2$
5.77	$1.287 \pm 0.003$	$102.1 \pm 0.2$
5.86	$1.299 \pm 0.003$	$103.1 \pm 0.2$
5.94	$1.313 \pm 0.004$	$104.2 \pm 0.3$
6.02	$1.320 \pm 0.004$	$104.7 \pm 0.3$
6.11	$1.333 \pm 0.004$	$105.8 \pm 0.3$
6.19	$1.354 \pm 0.004$	$107.5 \pm 0.3$
6.28	$1.359 \pm 0.004$	$107.9 \pm 0.3$
6.36	$1.375 \pm 0.004$	$109.2 \pm 0.3$
6.44	$1.386 \pm 0.004$	$110.1 \pm 0.3$
6.53	$1.393 \pm 0.005$	$110.6 \pm 0.4$
6.61	$1.408 \pm 0.005$	$111.8 \pm 0.4$
6.70	$1.419 \pm 0.005$	$112.7 \pm 0.4$
6.78	$1.429 \pm 0.006$	$113.6 \pm 0.5$
6.87	$1.452 \pm 0.006$	$115.0 \pm 0.5$



Cont. TABLE II

$\lambda(\text{\AA})$	$\ln T^{-1}$	$\sigma_H$ (barns)
6.95	$1.466 \pm 0.006$	$116.6 \pm 0.5$
7.04	$1.464 \pm 0.006$	$116.3 \pm 0.5$
7.12	$1.492 \pm 0.007$	$118.6 \pm 0.6$
7.21	$1.499 \pm 0.007$	$119.2 \pm 0.6$
7.29	$1.507 \pm 0.008$	$119.9 \pm 0.7$
7.37	$1.529 \pm 0.008$	$121.7 \pm 0.7$
7.46	$1.532 \pm 0.008$	$121.9 \pm 0.7$
7.54	$1.544 \pm 0.009$	$122.8 \pm 0.7$
7.63	$1.555 \pm 0.009$	$123.7 \pm 0.7$
7.71	$1.570 \pm 0.010$	$125.0 \pm 0.8$
7.80	$1.581 \pm 0.011$	$125.9 \pm 0.9$
7.88	$1.601 \pm 0.012$	$127.5 \pm 1.0$
7.96	$1.602 \pm 0.012$	$127.6 \pm 1.0$
8.09	$1.619 \pm 0.010$	$128.9 \pm 0.8$
8.25	$1.660 \pm 0.012$	$132.3 \pm 1.0$
8.43	$1.695 \pm 0.014$	$135.1 \pm 1.2$
8.60	$1.694 \pm 0.018$	$134.9 \pm 1.5$
8.81	$1.725 \pm 0.018$	$137.5 \pm 1.5$
9.06	$1.831 \pm 0.024$	$146.1 \pm 2.0$
9.36	$1.830 \pm 0.031$	$146.0 \pm 2.5$
9.70	$1.877 \pm 0.036$	$149.8 \pm 3.0$
10.03	$1.935 \pm 0.052$	$154.5 \pm 4.3$

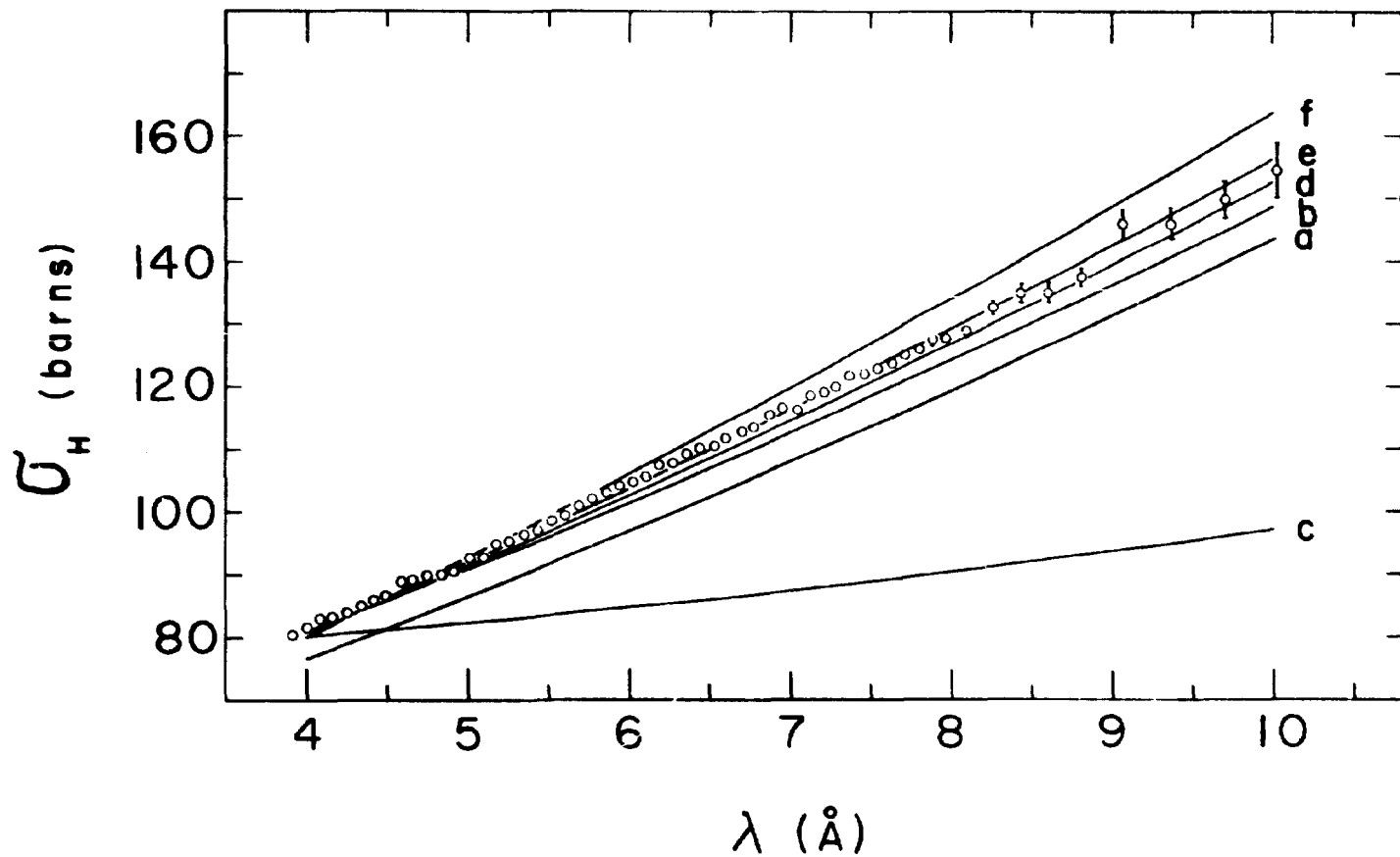


Fig. 1 - Scattering cross sections per hydrogen atom,  $\sigma_H$ , as a function of neutron wavelength,  $\lambda$ . Experimental points and calculated KN curve. — a ( $M_e = 9$ ,  $\bar{\omega} = 0.1 \text{ eV}$ ), b ( $M_e = 9$ ,  $\bar{\omega} = 0.3 \text{ eV}$ ), c ( $M_e = 64$ ,  $\bar{\omega} = 0.3 \text{ eV}$ ), d ( $M_e = 8$ ,  $\bar{\omega} = 0.3 \text{ eV}$ ), e ( $M_e = 7$ ,  $\bar{\omega} = 0.3 \text{ eV}$ ), f ( $M_e = 5$ ,  $\bar{\omega} = 0.3 \text{ eV}$ ).

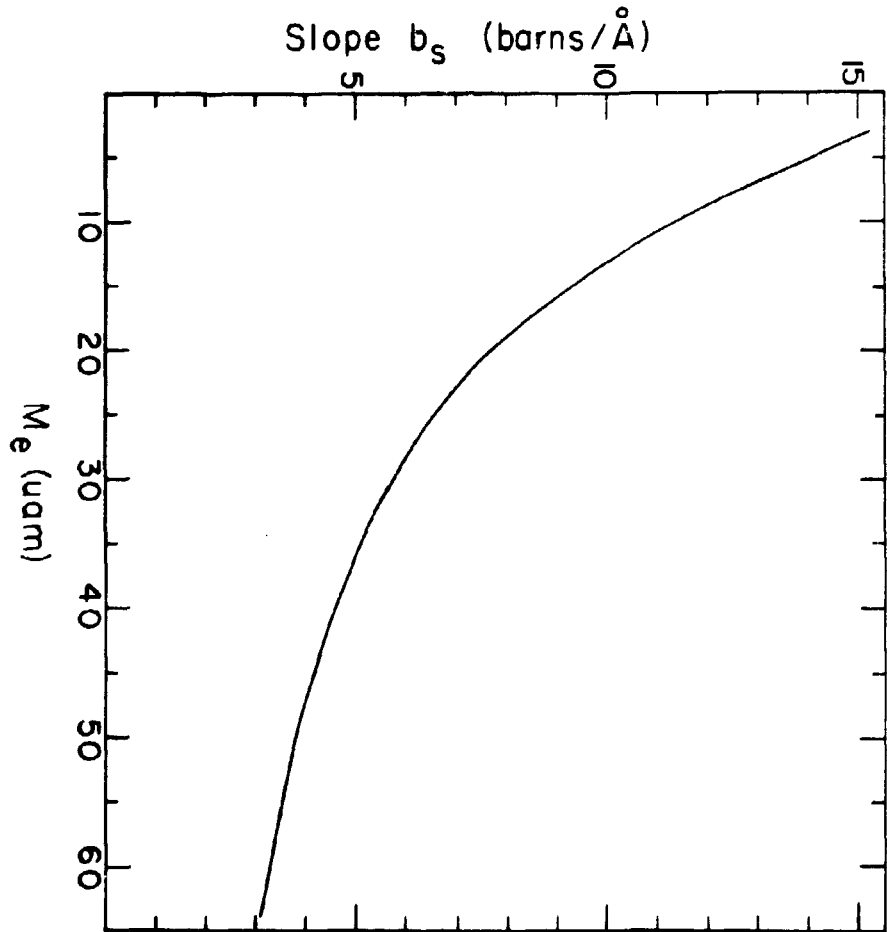


Fig 2 - Correlation between the effective proton mass  $M_e$  and the slope  $b_s$  obtained from the KN curves in the wavelength range 6Å to 10Å.

## RESUMO

Foi medida a secção de choque total do polidimetilsiloxano para neutrons com comprimento de onda  $\lambda$  no intervalo de 4 Å a 10 Å, na temperatura ambiente, usando-se um espectrômetro de tempo de voo com um "chopper" para neutrons lentos. Foram obtidas as secções de choque de espalhamento por átomo de hidrogênio,  $\sigma_H$ ; a inclinação da curva experimental  $\sigma_H \times \lambda$  resultou  $(12.2 \pm 0.2)$  barns/Å.

A comparação com  $\sigma_H$  calculado pelo formalismo de Krieger-Neikin para situações dinâmicas diferentes bem como a comparação com curvas de calibração relacionando a inclinação com a barreira que restringe a rotação interna, indica a existência de rotação praticamente livre dos grupos  $\text{CH}_3$  em torno do eixo  $\text{C}_3$ .

## RÉSUMÉ

On a mesuré la section efficace totale du polydiméthylsiloxane pour les neutrons avec longueur d'onde  $\lambda$  dans l'intervalle 4 Å à 10 Å, à la température ambiante, en utilisant un spectromètre à temps de vol avec un "chopper" pour neutrons lents. On a obtenu les sections efficaces de diffusion par atome d'hydrogène,  $\sigma_H$ ; l'inclinaison de la courbe expérimentale  $\sigma_H \times \lambda$  est  $(12.2 \pm 0.2)$  barns/Å.

La comparaison avec  $\sigma_H$  calculé par le formalisme de Krieger-Neikin pour de différentes situations dynamiques, aussi bien que la comparaison avec des courbes de calibration qui relient l'inclinaison avec la barrière qui restreint la rotation interne, indique l'existence de rotation pratiquement libre des groupes  $\text{CH}_3$  autour de l'axe  $\text{C}_3$ .

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