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A Study of Low Frequency Motions in Polyethylene and the Paraffin
Hydrocarbons by Neutron Inelastic Scattering*

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Abstract

The vibrational spectra between 800 and 30 cm^{-1} , derived from measurements of the time-of-flight distributions of initially "cold" neutrons inelastically scattered from thin samples, are presented for highly crystalline polyethylene at sample temperatures below and above both the glass transition and the melting point, and for samples of branched, irradiated, and quenched polyethylene at room temperature. The acoustical torsion mode ν_9 with a high frequency limit of 200 cm^{-1} and the acoustic deformation mode ν_5 with an estimated high frequency limit of 550 cm^{-1} are observed in agreement with the recent calculation by Tasumi, Shimanouchi, and Miyazawa of the normal modes of an infinite transplanar polyethylene chain. However, the measured spectra indicate that, although intermolecular forces appear to have a negligible influence, the distributions of frequencies associated with these modes are strongly influenced by the presence and by the phase of the disorder in the sample. Similar measurements for a series of n-paraffin hydrocarbons

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between C_6H_{14} and $C_{32}H_{66}$ at room temperature indicate that while nearly free internal rotations take place in the liquid phase, these rotations are hindered in the solid phase. As the length of the chain increases, the frequency distribution of the vibrational motions in the solid n-paraffins approaches that observed in polyethylene at room temperature.

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I INTRODUCTION

Polyethylene and the normal paraffin hydrocarbons have been studied extensively by infrared and Raman spectroscopy^(1,2), and by nuclear magnetic resonance measurements⁽³⁾, to determine the nature of their molecular motions. Nevertheless, these investigations have yielded only limited information about the low frequency motions; in polyethylene, for example, there has been no direct experimental determination of the spectra of molecular motions below 700 cm^{-1} . This region is of particular interest since recent theoretical calculations⁽⁴⁾ predict a clear separation in the vibrational spectrum of polyethylene with optical branches lying above 700 cm^{-1} and two acoustic modes lying below 500 cm^{-1} . Moreover, it is anticipated that a more detailed knowledge of the low frequency motions will yield a better understanding of the physical properties of this polymer.

In the present investigation the molecular motions with frequencies between 30 and 800 cm^{-1} in polyethylene and in the n-paraffins have been studied by measuring the energy distributions of initially "cold" neutrons which have been inelastically scattered from these samples.⁽⁵⁾ In this type of measurement, which has been described in the literature⁽⁶⁾, the incident low energy neutrons gain additional energy during the scattering process from the molecular motions of the sample. Because of the large incoherent cross section of hydrogen, this scattering is, to a good approximation, completely incoherent and isotropic for the samples investigated. For an incoherent scatterer the probability that a neutron gains an energy $\Delta E = h\nu$ is linearly related to the density of vibration modes of frequency ν . Consequently, the scattering

contains information about all the molecular motions in which the hydrogen atoms participate and is not limited by selection rules or symmetry considerations as in the case of optical measurements. Thus, these measurements not only complement the frequency regions accessible to infrared and Raman measurements but allow a more direct comparison between theory and experiment.

A systematic investigation of low frequency motions has been made. The molecular motions in highly crystalline polyethylene have been investigated as a function of the sample temperature with particular emphasis on the changes observed in these motions above and below both the glass transition and the melting point. In addition, the neutron spectra from branched, quenched, and irradiated samples have been measured in an effort to understand, at least qualitatively, the influence of various physical treatments on these motions. Finally, the spectra from a series of six n-paraffins between C_6H_{14} and $C_{32}H_{66}$ were measured to compare the motions in short chains in both the liquid and the solid phase with those observed in polyethylene, and to allow a comparison with previous Raman measurements within the frequency range of the present experiment.

II THEORY

Two types of motion are possible in polyethylene: vibrations, which are defined to include the cooperative torsional oscillations that a chain in a given isomeric configuration can execute, and internal rotations, which give rise to the multitude of rotational isomeric configurations that the chain can assume. Translations and rotations

of the molecule as a whole may be excluded because of its large size.

At low temperatures, where only vibrations need be considered, it is possible, in principle, to give a complete description of the motions in a polyethylene chain in terms of its normal modes. However, to date all calculations of these normal modes in polyethylene have been confined to the extended chain configuration because only in this case are the secular equations computationally tractable. Although a number of such calculations have appeared in the literature⁽⁷⁻⁹⁾, only the recent treatment by Tasumi, Shimanouchi, and Miyazawa⁽⁴⁾ (hereinafter abbreviated as TSM) will be considered here for a comparison with experiment. These authors have reported a complete normal coordinate calculation for an infinite polyethylene chain based on a semi-empirical set of Urey-Bradley force constants and subject to the assumption that the frequencies of the normal vibrations are determined primarily by the intramolecular force field. Despite this specialization the results obtained are in a form particularly suited to the present investigation since they have calculated dispersion curves for all of the vibrational modes.

The treatment of TSM predicts nine vibrational modes: five (ν_1 - ν_5) are symmetric and four (ν_6 - ν_9) are antisymmetric with respect to the skeletal plane. Of these, two, ν_5 and ν_9 , are acoustic modes. ν_5 , with a high frequency limit at 500 cm^{-1} , is a combination of the skeletal stretching and bending normal modes, while ν_9 corresponds to a skeletal torsional vibration of the chain and has a high frequency limit at about 190 cm^{-1} . The remaining modes are optical branches lying above

700 cm^{-1} . For each of the nine modes, the frequency is given as a function of the phase difference $\delta = k\pi/(N+1)$ ($k = 1, 2, \dots, N$) between two adjacent methylene groups, where N is the number of methylene groups in the chain. Thus in a finite chain of length N , each mode consists of a band of N discrete frequencies. For an infinite chain ($N \rightarrow \infty$) the dispersion relations become continuous functions of the phase difference. The dispersion curves for the two acoustic modes and the two lowest optical branches are reproduced in Fig. 1.

Neither of the acoustic modes predicted by TSM is observed in the infrared and Raman spectra of polyethylene because their active phases have zero frequency. However, Raman measurements have provided a partial verification of the existence of the mode ν_5 in the solid paraffins (C_4H_{10} to $\text{C}_{16}\text{H}_{34}$), where the lowest line observed in each spectrum has been shown to correspond to the frequency of the active phase ($k = 1$) of this mode. As yet, there has been no direct experimental evidence concerning the torsional mode ν_9 . In the present measurements, the absence of selection rules and symmetry limitations allows the entire frequency distribution of these modes to be observed and thus provides a more direct comparison with the theory.

The above results are expected to be valid only for 100% crystalline polyethylene well below its melting point where the individual chains are all in their extended trans-configuration. It should be noted that crystallinity per se is not a requirement; since intermolecular forces have been neglected, all the theory requires is that the chains are and remain extended, i.e., that there are no transitions

between different isomeric configurations (internal rotation). However, real samples of polyethylene are semi-crystalline, containing both ordered and disordered "regions". Both specific heat data^(10,11) and nuclear magnetic resonance measurements⁽³⁾ indicate that hindered internal rotations occur in disordered regions at temperatures much below the melting point; it is the onset of these rotations that defines the glass transition interval ($120^{\circ}\text{K} - 250^{\circ}\text{K}$).⁽¹²⁾ Both the existence of chains in non-trans configurations and the coupling between vibrational and rotational motions may be expected to cause departures from the theory, and it is the low frequency acoustic modes that should be most sensitive to these changes.

The torsional mode ν_9 and internal rotation in a polyethylene chain are both associated with the relative rotation of adjacent C-C-C groups with respect to one another about the C-C bond joining them. Such rotations are impeded by hindering potentials and the rotation about a given bond depends significantly on the state of the neighboring bonds. For an extended trans-planar chain at low temperatures the hindering potential for rotation about a given bond exhibits three minima: an absolute minimum corresponding to the trans state and two relative minima, higher by about 800 cal/mole, corresponding to the two gauche states. Torsional oscillations take place about the central minima and transitions from trans to gauche states are highly improbable. As the excitation energy kT is increased, the latter transitions are expected to occur with increasing probability thereby decreasing the probability of the torsional oscillations associated with a given isomeric configuration. In crystalline polyethylene, the

chain configurations are almost exclusively trans at room temperature, whereas just above the melting point at 411°K estimates show that 35% of the bonds are in the gauche rotational states. ⁽¹³⁾

III EXPERIMENTAL METHOD

A. Instrumentation

The data in this investigation were obtained using the Brookhaven slow chopper, which has been described in detail in the literature. ⁽⁶⁾ Its essential features may be briefly summarized as follows. A coarsely collimated neutron beam emerging from the pile traverses eight inches of refrigerated polycrystalline beryllium before striking the sample. The Be serves as a low pass filter effectively transmitting only those neutrons with energies (≤ 5.2 milli-electron volts (meV)). Below this sharply defined cut-off energy, the Maxwellian distribution of the pile neutrons decreases rapidly, so that the energy distribution in the incident beam is asymmetric with a full-width at half-maximum equal to approximately 1 meV. Neutrons scattered by the sample in the direction θ with respect to the incident beam are chopped into bursts by a rotating element. Their velocity, and hence energy, distribution is determined by measuring their flight times over a five meter flight path between chopper and detector on a 256-channel analyzer. The data, thus obtained, are corrected for background, chopper transmission, and detector efficiency, all of which are energy dependent. The incident beam intensity is continuously monitored allowing different sets of data to be normalized to the same relative incident neutron intensity.

In the present measurements, thin samples (0.7 - 0.8 mm of

polyethylene) were employed so that the effects of multiple scattering would be small. In the case of the n-paraffins somewhat thicker samples were used. While no attempt has been made to correct for the multiple scattering in these samples, its influence at three representative energies is estimated in Fig. 2 as a function of the effective sample thickness, n_H , the number of hydrogen atoms per cm^2 . Although these curves were derived from the data of Larsson et al⁽¹⁴⁾ for water, comparison of the observed scattering from two samples of liquid $n\text{-C}_6\text{H}_{14}$, differing in thickness by a factor of 10 (0.3 and 3.0 mm), indicate that the estimates shown are approximately correct for the samples investigated in the present study.

All of the distributions presented in the following section were obtained for a scattering angle $\theta = 90^\circ$. The observed intensity is (neglecting multiple scattering) proportional to the differential scattering cross section $(d^2\sigma/d\Omega dE)(dE/dt)$. The factor (dE/dt) appears since the neutron's final energy is determined by its flight-time t . While $d^2\sigma/d\Omega dE$ is in general a complicated function, a number of simplifications are possible in the present experiment. First, the experimental arrangement allows only the elastic scattering ($E = E_0$) and the inelastic scattering ($E > E_0$) corresponding to neutron energy gain to be observed. Second, due to the relatively large incoherent scattering length for hydrogen, only the incoherent scattering cross section need be considered. Finally, when the initial neutron energy is small compared to both kT and the level spacing of the vibrations investigated, it can be assumed that the energy gained by the neutron is acquired by the annihilation of a single phonon. The incoherent

differential one-phonon cross section is linearly related to $g(h\nu)$, the number of frequencies between ν and $\nu + d\nu$.⁽¹⁵⁾ Moreover, the functional form of this cross section is sufficiently simple to allow $g(h\nu)$ to be derived from the time-of-flight distributions of the present experiment. However, at high temperatures where multiphonon scattering may not be negligible, the frequency distribution $g(h\nu)$ obtained by the above procedure will be of doubtful significance.

B. Sample Preparation

The physical characteristics of the samples used in the present experiment are summarized in Table I. Also listed are the actual and effective thicknesses of the samples. The latter, given in terms of the number of hydrogen atoms per cm^2 , is included to allow an estimate of the multiple scattering to be expected in the various measurements (see Fig. 2).

Square plates (15 x 15 x 0.08 cm) of highly crystalline polyethylene (PE-0) were prepared from Phillips Marlex 6050 pellets pressed with 30 tons at 138°C for six minutes and then slowly cooled to ambient temperature. Two branched polyethylene samples (PE-1 and PE-2) of lower crystallinity were prepared in a similar manner from material synthesized using appropriate catalysts. One sample of PE-0 was irradiated with a dose of 2.8×10^6 rads of Co^{60} γ -rays to produce an estimated 3-5 cross-links per chain. Finally, quenched samples of PE-0 were obtained by pressing Marlex 6050 pellets 4-5 minutes at 155°C and then rapidly cooling the plates to -80°C.

In the preparation of the above polymers, the catalyst residues were removed by appropriate de-ashing procedures and all samples

were pure within the limits of infrared spectra. The sample of PE-0 used in the high temperature measurements was sealed in an aluminum foil although no attempt was made to exclude trapped air. Examination of this sample at the conclusion of the runs indicated that some annealing had taken place during the measurements. However, intrinsic viscosity measurements showed that no measurable cross-linking or chain scission had occurred.

In the case of the n-paraffin series, the samples of $C_{20}H_{42}$ and $C_{32}H_{66}$ were Eastman white label (EWL) grade. The remaining samples in the series were Eastman practical (P) grade.

IV EXPERIMENTAL RESULTS

A. Polyethylene

The time-of-flight distribution of neutrons scattered from a highly crystalline sample of polyethylene (PE-0; $d = 0.96 \text{ gm/cm}^3$) at room temperature is shown in Fig. 3a. Here, as in subsequent cases, the corrected number of counts per time channel is plotted on an arbitrary scale as a function of the channel number. The corresponding neutron energy scale is appended. Figure 3b shows the frequency distribution derived from this data in the one-phonon approximation. The horizontal hatched bars represent the dispersions calculated by TSM for the modes in the frequency range $0\text{-}1500 \text{ cm}^{-1}$.

In Fig. 3a, the sharp rise in the distribution at 5.2 meV followed by the more gradual decrease at lower energies constitutes the elastic scattering from the sample and this shape reflects the energy distribution in the incident beam. Four instrumental peaks are visible in

this region: two, at 6.8 and 6.4 meV, are due to secondary Bragg cut-offs in Be, and two, at 5.0 and 3.7 meV, are due to Bragg cut-offs in aluminum. The inelastic distribution above 5.2 meV, which is related to the spectrum of molecular motions in the sample, is seen to be the superposition of a number of components. The most pronounced features of this spectrum are (E) the peak at 20 meV⁽¹⁶⁾, which is sharply terminated on its high energy side, (D) the rise below 55 meV to the shoulder at 29 meV, and (B) a second shoulder at 88 meV. Less pronounced are two reproducible changes in slope (C) and (A) at 60 and 150 meV respectively. Below 20 meV the distribution decreases irregularly and the slight shoulder between 14 and 16 meV suggests the presence of another component (F) in this region.

The various components in the time-of-flight distribution are best compared with the predictions of TSM by considering the derived frequency distribution in Fig. 3b. The shape of the peak E is characteristic of an acoustic mode and, allowing for instrument resolution, exhibits a high frequency limit fairly well defined at 200 cm^{-1} . This is in good agreement with the calculated limit (190 cm^{-1}) of the torsional mode ν_9 . The partially resolved peak at 720 cm^{-1} , which corresponds to B the 88 meV shoulder in Fig. 3a, correlates well with the lowest optical mode ν_8 . The broad peak A centered at about 1350 cm^{-1} is probably associated with the higher optical modes which are unresolved because of overlap and poor instrument resolution at higher energies.

The remaining three components are also discernable in the frequency distribution. The slight rise C between 550 and 450 cm^{-1}

is not well resolved and is further obscured by the broad component D which rises steeply below 400 cm^{-1} . The slight shoulder near 90 cm^{-1} corresponds to F in Fig. 3a. Thus, below 600 cm^{-1} four components appear in the frequency distribution of PE-0 at room temperature.

The existence of the above four distinct components below 600 cm^{-1} in the neutron spectrum of highly crystalline polyethylene is more clearly indicated at low temperature. Figure 4a shows the energy distribution obtained from a second sample of PE-0 at 100°K , which is well below the glass transition. The energy distribution of Fig. 3a is reproduced (dashed curve) for comparison. The reduction in thermal motion at low temperature is evident in the relative intensities of the inelastic and the elastic scattering, and by the negligible amount of scattering from the optical modes. The significant feature, however, is that the shape of the distribution is altered to such an extent that the four components observed below 600 cm^{-1} at room temperature are better resolved. The relative changes occurring in the individual components as the temperature is lowered is most easily seen by comparing the low temperature frequency distribution shown in Fig. 4b with that of Fig. 3b. This comparison shows that, while E still defines a high frequency cut-off near 200 cm^{-1} , both D and F exhibit pronounced changes in shape and tend to peak at 340 and 130 cm^{-1} , respectively. The component C also exhibits an altered shape at low temperature and may be interpreted as defining a high frequency cut-off between 500 and 600 cm^{-1} . The latter is not well defined because the instrument resolution decreases with increasing energy transfer and because of the

low statistical accuracy of the data in this frequency range. Finally, there is some indication of a fifth weak component G in the region 50-70 cm^{-1} (6-9 meV in Fig. 4a).

The energy distributions from a third sample of PE-0 as a function of increasing sample temperature and their corresponding frequency distributions are shown in Figs. 5 and 6, respectively. The measurements were performed in the following sequence: 293, 468, 428, and 412°K, the latter temperature being very close to the melting point of the sample. In Fig. 5 the increase in intensity at 412°K reflects the increase in molecular motion due to thermal excitation. Again, the relative shape of the spectrum is visibly altered. There is a pronounced increase in the intensity of the component (D), while the contribution of (E) has actually decreased. The relative changes in these two components is even more pronounced at the higher temperatures; at 195°C (E) has lost its identity. It is also interesting to observe that $D(\nu_8)$ is not resolved at the middle temperatures but reappears at the highest temperature. This behavior is associated with the general reduction in intensity observed above 428°K and suggests that the character of the motions below 600 cm^{-1} are further altered between 428°K and 468°K.

A significant feature of the time-of-flight distributions obtained from polyethylene above the melt is that there is (within experimental error) no elastic peak. The residual rise at 5 meV is due to the (200) Bragg cut-off in the Al of the chopper. The absence of an elastic peak implies that above the melting point there exists a dense closely-spaced level system for the entire sample, such that

the multi-phonon scattering cross section approaches the "classical limit" and is a monotonically decreasing function of the neutron energy through E_0 . This level system also accounts for the substantial increase in the scattering at low energies observed at 155°C.

The influence of branching on the low frequency motions in polyethylene is shown in Fig. 7, where the neutron spectra obtained from the two samples PE-1 and PE-2 ($d = 0.945$ and 0.916 gm/cm³, respectively) are compared with that obtained from PE-0. Figure 8 shows a comparison of the neutron spectra obtained from virgin, quenched, and irradiated samples of PE-0. In both figures the spectra have been normalized to the same number of hydrogen atoms per cm² to compensate for the differences in thickness of the samples employed. Differences in the amount of multiple scattering present in these samples is estimated to be less than 10 per cent. (see Fig. 1)

The observed changes in the spectrum with increased branching are similar to the changes observed in the spectrum of PE-0 as a function of increasing temperature. There are, however, differences. The spectrum of PE-1 shows a pronounced increase in intensity due primarily to an increase in the contribution of the component D. But in this case E is not appreciably diminished, although its shape is somewhat sharpened on the low energy side. The spectrum of PE-2 shows that as the number of branches is further increased there is a general reduction in the scattering at higher energies accompanied by an increase in the scattering at the low energies. Moreover, (E) is considerably broadened and does not exhibit a well-defined high frequency limit. In the case of the irradiated sample, the spectrum exhibits the same

features as those observed in PE-1, i.e.: an increase in D and a slight sharpening of E.

B. n-Paraffins

The time-of-flight distributions of neutrons scattered at 90° from a series of six n-paraffins at room temperature are shown in Fig. 9. The first three (C_6H_{14} , $C_{12}H_{26}$, $C_{16}H_{34}$) are liquids and the remaining three ($C_{18}H_{38}$, $C_{20}H_{42}$, $C_{32}H_{66}$) are solids at this temperature. Figure 10 shows the frequency distributions, derived in the one-phonon approximation, of the motions below 850 cm^{-1} in the two solids $C_{20}H_{42}$ and $C_{32}H_{66}$.

The spectra of the liquid paraffins in Fig. 9 are similar to the spectrum of PE-0 above its melting point, and are characterized by a broad distribution of inelastically scattered neutrons peaked slightly above kT and by the absence of an elastic peak. In addition, a weak component is visible at about 180 cm^{-1} in each of the three spectra. The spectra of the solid paraffins, on the other hand, all show a pronounced elastic peak and an inelastic distribution similar to those obtained from PE-0 below the melt. The two principal components comprising the latter occur at approximately 240 and 170 cm^{-1} and become more pronounced as N increases.

The frequency distribution of the motions in $C_{32}H_{66}$ (Fig. 10) shows a striking similarity to the frequency distribution of the motions in PE-0 at room temperature (Fig. 6). The maxima at 720 and 190 cm^{-1} are readily identified as the contributions from the modes ν_8 and ν_9 respectively. In addition, the weak peak at 480 cm^{-1}

followed by the steeper rise between 400 and 240 cm^{-1} indicates the presence of the two components C and D in this frequency range.

In comparison, the frequency distribution of the motions in $\text{C}_{20}\text{H}_{42}$ does not show these components as distinctly and its general shape more closely resembles the frequency distribution of PE-0 at 412°K .

DISCUSSION

A. Polyethylene

The agreement between the observed high frequency limits at $200 \pm 15\text{ cm}^{-1}$ and $550 \pm 50\text{ cm}^{-1}$ in the frequency distribution of PE-0 at 100°K (Fig. 4b) and the limits of 190 cm^{-1} and 500 cm^{-1} calculated by TSM for the acoustic modes ν_9 and ν_5 , respectively, may be taken as confirmation of the existence of these modes in highly crystalline polyethylene. However, the additional broad peaks (D, F, and G) centered at 340, 130, and 60 cm^{-1} , respectively, appear in the distribution. Thus, even though the sample is predominantly crystalline and at a temperature where only vibrations are known to occur^(11,12) the entire observed frequency cannot be accounted for by the simple superposition of these two modes using the Debye approximation and the derived dispersion curves. Therefore, it appears that disorder in the sample may have an appreciable influence on the vibrational chain motions.

Although the three-dimensional morphology of highly crystalline polyethylene is, at present, the subject of considerable debate, one may think of the individual macromolecules as comprised of relatively long trans-planar segments ($N = 50 - 100$), where the chain is defined to be ordered, connected by series of one or more shorter gauche-linked

segments where the chain is defined to be disordered.⁽¹⁷⁾ Indirect experimental information about the size of the short chain segments in semi-crystalline polyethylene has been provided by nuclear magnetic resonance measurements.⁽³⁾ The γ process, ascribed to internal rotations of 3-5 CH_2 units in the disordered regions, is observed to set in at about 175°K . This suggests that at lower temperatures ($T < 120^\circ\text{K}$) where internal rotations are "frozen" out, the disordered portions of the chain consist of segments that not only are short but have an average length $N = 4$. It seems reasonable to assume that at low temperatures these short segments are also in the trans-planar configuration since this is the configuration of minimum potential energy.

According to the theory of TSM, the dispersion relations of ν_5 and ν_9 for a chain segment of length N are no longer continuous functions of the phase δ , but discrete sets of N frequencies corresponding to the values $\delta = k\pi/(N+1)$.⁽¹⁸⁾ When N is large the frequencies are sufficiently closely spaced so that the continuous dispersion relations represent a good approximation of the distribution of vibrational frequencies. On the other hand, for $N = 4$ the discrete frequencies comprising the modes ν_5 and ν_9 are 340, 500, 330, 80 cm^{-1} and 125, 180, 150, and 47 cm^{-1} respectively, corresponding to the phases $\delta = \pi/5, 2\pi/5, 3\pi/5, 4\pi/5$ (see Fig. 2).

Strictly speaking, the application of the theory to individual segments is valid only if the segments are rigidly terminated. Such a concept is physically unrealistic; some coupling between connected segments must occur to allow energy to be distributed along the chain.

It is therefore assumed that although the gauche links do not participate freely in cooperative vibrations and damp all vibrational frequencies which require them to move with an appreciable amplitude, they can execute restricted motion. This restricted motion will allow frequency bands centered about the above discrete frequencies to be propagated by the short ($\bar{N} = 4$) segments, the bands being broader at lower frequencies. Hence, the superposition of the modes ν_5 and ν_9 for chains consisting of coupled long ($N > 50$) and short ($\bar{N} = 4$) segments will produce peaks in the frequency distribution at approximately 500, 335, 180, 135, and 65 cm^{-1} in qualitative agreement with observation.

The above model for polyethylene is most certainly an oversimplification and is offered here only as a possible explanation which correlates the data of the present investigation with the theory of TSM. Nevertheless, the agreement between theory and experiment suggests that the normal modes of the chains in semicrystalline polyethylene are strongly influenced through coupling by relatively small amounts of disorder (as defined above) along the chains. It should also be re-emphasized that nowhere does crystallinity per se enter the argument; the fact that the observed frequency distribution down to 30 cm^{-1} can be accounted for with a one-dimensional model implies that intermolecular forces are even less important than might have been anticipated.

At room temperature, which is well above the glass transition, internal rotations are operative along the disordered portions of the chains in semicrystalline polyethylene. However, these rotations

are strongly hindered. Nuclear magnetic resonance^(3,19) measurements indicate that the transitions between different isomeric configurations take place in 10^{-5} - 10^{-7} seconds in the temperature range 240°K - 293°K . In contrast, the neutron interaction time is of the order of 10^{-12} seconds⁽²⁰⁾ and the probability of directly observing internal rotations in this temperature range is so small that it may be neglected. Consequently, despite the presence of hindered internal rotations, the frequency distribution below 600 cm^{-1} of PE-0 at 293°K (Fig. 3b) still represents to a good approximation, a vibrational spectrum with the acoustic modes ν_5 and ν_9 visibly modified.

These changes in this spectrum are attributed to changes in the coupling between the vibrations of the long and short chain segments introduced by the onset of internal rotations of the latter. It is of interest to note that the two modes are affected in different ways. The high frequencies of the torsional mode appear to be more easily propagated (i.e., less damped) than the lower frequencies; indeed ν_9 exhibits a nearly linear frequency distribution rather than a nearly constant distribution predicted by the theory for an infinite trans-planar polyethylene chain. The high frequencies of ν_5 , on the other hand, appear strongly suppressed, there being no clear indication of its high frequency limit at room temperature. Moreover, the component D is shifted to lower frequencies. It is possible that the observed changes in ν_5 are due in part to a splitting of the skeletal vibrational levels resulting from vibration-rotation coupling in the disorder segments, which further modifies the "boundary

conditions¹¹ of the long segments.

The time-of-flight distributions obtained from PE-0 near and above the melting point (Fig. 5) exhibit further changes due to the spread of internal rotations into the ordered (long segments) portions of the chains. The pronounced decrease in the relative intensity of the ν_9 at 412°K indicates that cooperative torsional oscillations are giving way to internal rotations. Thus at 428°K, multiphonon scattering from nearly free rotations causes the substantial increase in low energy scattering and reduces the elastic peak. The presence of multiphonon processes casts doubt on the validity of the corresponding frequency distributions (Fig. 6) since they are derived in the one-phonon approximation. Nevertheless, the evolution of the frequency distribution into two broad peaks at 260 cm⁻¹ (ν_5) and 180 cm⁻¹ (internal rotations) at the highest temperature measured appears to have some significance, since one expects skeletal vibrations to persist as long as the macromolecules retain their identity.

The observed changes in the neutron spectra of polyethylene with increased branching (Fig. 7) appear similar to the changes observed in the spectra of PE-0 as a function of increasing temperature. The spectrum of PE-1 shows a pronounced increase in the intensity of ν_5 and a reduction in the relative intensity of ν_9 . The fact that the latter appears somewhat sharper on its low energy (long wavelength) side is consistent with the notion that the pendant methyl groups limit the lengths of the ordered chain segments. As the number of the branches is further increased (PE-2) there is a

general reduction in the scattering at high energies accompanied by an increase in the scattering at low energies. Moreover, ν_9 is considerably broadened. These changes suggest that, at least in portions of the chains, internal rotations have become much less hindered. The fact that a few per cent branching produces such pronounced changes illustrates the sensitivity of the low frequency chain vibrations in polyethylene to limited internal rotations along the chains.

The neutron spectrum of the irradiated polyethylene sample (Fig. 8) is intermediate to PE-0 and PE-1, showing some increase in the intensity of ν_5 and a slight sharpening of ν_9 . This similarity suggests that as long as their number is small, cross-links and branches affect the low frequency vibrations in an analogous manner. The spectrum of quenched PE-0 also indicates some increase in disorder along the chains, although the fact that ν_9 remains well defined implies that a relatively high degree of linear order is established despite rapid cooling. It should be noted that quenching, although it may reduce crystallinity in polyethylene, does not produce radical changes in the neutron spectrum. This is consistent with the assumption that the present data can be accounted for by the theory of TSM and that intermolecular forces are negligible.

B. n-Paraffins

The neutron spectra of the n-paraffins at room temperature (Fig. 9) exhibit changes with increasing N similar to those observed in the spectrum of highly crystalline polyethylene as its temperature is lowered through the melting point. The broad inelastic distribution

peaking near kT and the absence of an elastic peak, which characterize the liquid paraffin spectra, are indicative of multiphonon scattering from a nearly continuous level system which is appreciably populated. As in the case of polyethylene above 412°K , this scattering is attributed to interactions with nearly free internal rotations which take place along the entire length of the molecules.

The appearance of an elastic peak in the spectra of the solid n -paraffins reflects an increase in the rigidity of the molecules resulting from an increase in the hindrance to internal rotations. This behavior suggests a possible correlation between the length of the chain and the height of the hindering potentials for internal rotations such that at room temperature the additional increment in chain length in going from cetane to octadecane produces a relatively abrupt increase in the rotational barriers. As N approaches 32, the frequency distribution (Fig. 10) shows the evolution of the torsional mode ν_9 together with identifiable contributions from ν_5 similar to those observed for PE-0 at room temperature.

Raman spectra of the solid n -paraffins exhibit a single line below 500 cm^{-1} the frequency of which varies from 425 cm^{-1} in butane to 150 cm^{-1} hexadecane.⁽²⁾ In each case the frequency of this line is in good agreement with the active phase ($k = 1$) of the skeletal deformation mode ν_5 .⁽⁴⁾ It has been suggested⁽²⁾ on the basis of these measurements that in the solid phase the molecules of the n -paraffins are in the extended configuration. The present measurements, which yield the entire frequency distribution indicate that in the solid paraffins some degree of rotation persists at room temperature.⁽²¹⁾ However,

the extent to which the methyl end groups contribute to the observed spectra and influence the internal rotation of adjacent chain segments is uncertain. It is hoped that further detailed measurements of the neutron spectra of the n-paraffins as a function of both N and temperature will provide more specific information about the role of terminal methyl groups.

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15. In the one-phonon approximation, the incoherent cross section for neutron energy gain is given by

$$\frac{d^2\sigma}{d\Omega d\epsilon_{\text{incoh}}} = (\text{constant}) a_{\text{incoh}}^2 \frac{k}{k_0} \frac{h^2(\vec{k}_0 - \vec{k})^2}{h\nu} \frac{e^{-2W}}{e^{+h\nu/k_B T} - 1} g(h\nu)$$

where a_{incoh}^2 is the incoherent cross section for the hydrogen atom, $\vec{k}_0$ and $\vec{k}$ are the initial and final wave vectors of the neutron, and e^{-2W} is the Debye-Waller factor, assumed to be a constant in the present calculations. For a more detailed discussion see L. S. Kothari and T. S. Singwi, "Advances in Research and Application" in Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press Inc. New York, 1959) Vol. 8, p. 109.

16. The energy values quoted when referring to the inelastic components correspond to actual energy transfers and are approximately 5 meV lower than their positions on the neutron energy scale. The corresponding frequencies may be obtained by multiplying the values quoted by 8.
17. This definition of order and disorder along a chain is compatible with the Fringe-micelle, folded chain, or distributed defect descriptions of the morphology of semi-crystalline polyethylene.
18. It should be noted that here we are considering a segment of an effectively infinite chain. The discrete frequencies associated with a finite chain of length N will be different.
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20. Both nuclear magnetic resonance measurements and neutron scattering measurements are sensitive to proton motions. However, because of the difference in "observation" time the two experimental methods complement one another.

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FIGURE CAPTIONS

Figure 1. Deviations in the intensity of scattered neutrons due to multiple scattering as a function of the effective sample thickness for three typical scattered neutron energies. The curves have been normalized such that zero sample thickness and hence zero multiple scattering corresponds to unit intensity.

Figure 2. Dispersion curves ν vs. δ , the phase between adjacent CH_2 units, for the four lowest vibrational modes ν_4 , ν_8 , ν_5 , and ν_9 in an infinite transplanar polyethylene as predicted by the theory of TSM.

Figure 3(a) Time-of-flight distribution of neutrons scattered at $\theta = 90^\circ$ from a sample of Marlex 6050 at room temperature. Four instrumental peaks appear in the region of the elastic peak (see text). (b) Frequency distribution derived from the data of (a) in the one-phonon approximation. The horizontal hatched bars show the calculated dispersions of the modes between $0\text{-}1500\text{ cm}^{-1}$ as given by TSM. The arrows indicate the components A through F as discussed in the text.

Figure 4(a) Time-of-flight distribution of neutrons scattered at $\theta = 90^\circ$ from a sample of Marlex 6050 at 100°K . The distribution of Figure 3(a) is shown (dashed curve) for comparison. (b) The frequency distribution derived from the data of (a) in the one-phonon approximation. $\hbar\omega$ is the phonon energy. The vertical arrows pointing upward give the frequencies for $N = 4$ for ν_5 and ν_9 as described in the text.

Figure 5. The time-of-flight distributions of neutrons scattered from a sample of Marlex 6050 at four different temperatures near and above the melt temperature (411°K)

Figure 6. The frequency distributions derived from the data of Fig. 5 in the one-phonon approximation.

Figure 7. The time-of-flight distributions of neutrons scattered from three samples of polyethylene possessing varying degrees of branching (see text).

Figure 8. The neutron time-of-flight spectra for samples of virgin, quenched, and irradiated Marlex 6050.

Figure 9. The time-of-flight distributions of neutrons scattered at 90° from six n-paraffin hydrocarbons. The first three (C_6H_{14} , $\text{C}_{12}\text{H}_{26}$, $\text{C}_{16}\text{H}_{34}$) are liquid and the last three ($\text{C}_{18}\text{H}_{38}$, $\text{C}_{20}\text{H}_{42}$, $\text{C}_{32}\text{H}_{66}$) are solid at room temperature, the temperature at which the measurements were made.

Figure 10. The frequency distributions of motions in $\text{C}_{20}\text{H}_{42}$ and $\text{C}_{32}\text{H}_{66}$ derived from data of Fig. 9 in the one-phonon approximation.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

FIGURE 6

FIGURE 7

FIGURE 8

FIGURE 9

FIGURE 10

TABLE I. PHYSICAL CHARACTERISTICS OF SAMPLES INVESTIGATED

SAMPLE	DENSITY (g/cm ³)	CRYSTALLINITY (%)	BRANCHING (%) OR GRADE	SAMPLE THICKNESS (cm)	n _H (H/cm ²)
PE-0 ^a	0.960	85 ^b	0.13 ^d	0.08	0.6x10 ²²
PE-1	0.945	70 ^b	0.33 ^d	0.10	0.8
PE-2	0.916	45 ^b	3.8 ^d	0.08	0.6
n-C ₆ H ₁₄		liquid ^c	P	0.30	1.9
n-C ₁₂ H ₂₆		liquid ^c	P	0.30	2.1
n-C ₁₆ H ₃₄		liquid ^c	P	0.30	2.1
n-C ₁₈ H ₃₈		solid ^c	P	0.20	1.4
n-C ₂₀ H ₄₂		solid ^c	EWL	0.20	1.4
n-C ₃₂ H ₆₆		solid ^c	EWL	0.14	1.0

a. Phillips Marlex 6050

b. Estimates based on the measured densities

c. At room temperature

d. Assuming 100% methyl branching