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Influence of Viscoelasticity of Amorphous Layers on Longitudinal Accordion Mode Scattering of Polymers

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The normal viscoelasticity of the amorphous component yields a rapid exponential decrease of the amplitude of the longitudinal accordion type oscillations in the defect areas of the macromolecule in the crystalline core and in the amorphous layers on the folds containing surfaces of the lamellae. The macromolecule in the amorphous layer and in crystal defects changes direction and, hence, cannot conserve the longitudinal oscillation. The jumping of this oscillation to neighboring molecules accelerates so much its decrease that the straight sections between the two surface layers are longitudinally completely, while those between any two defects, or between one defect and the surface layer nearly completely decoupled from the rest of the sample. The effect is enhanced by the fact that the basic wave length of the observed Raman scattering is a little smaller than twice the length of the oscillating straight section. Maximum of the vibration energy occurs inside these sections and not in the amorphous regions. Since the lateral decoupling is guaranteed by the smallness of lateral forces, each straight section oscillates as if it were completely independent of the short and long range crystalline and amorphous environment. Only in such a case a simple conclusion on the distribution of straight chain sections can be deduced from the experiment.

INTRODUCTION

The linear accordion mode (LAM) Raman scattering of straight sections of dissolved linear paraffins has been known for a long while since its discovery and interpretation in terms of normal mode oscillations of the randomly coiled molecule by Schimanouchi et al.^{1,2} It was used for the measurement of the length and fraction of straight sections of the randomly coiled linear molecule in solution or melt. A basic improvement was made by using the more monochromatic LASER light source^{3,4} (ALR = accordion type laser-Raman scattering) which also permitted the investigation of higher harmonics, up to the 31-st order, of the crystallized fully stretched paraffin molecules which have up to 94 C-groups. Since these molecules do not yet fold they are much longer than the straight sections in melted or dissolved paraffins. One actually measures the length L_R of the molecules which may be tilted by a fixed angle θ to the normal of the large surface of lamellar crystals. In such a case the distance D of these surfaces is usually a little shorter than $L_R = D/\cos \theta$.

The application to folded polymers was difficult. The experiments on first samples of solid polyethylene (PE) were refused with the excuse that the molecular weight is much too high to be investigated by LAM scattering. The spectroscopist asked for cooperation did not know about the small finite thickness between 100 and 200 Å of polymer crystals. This thickness contains almost straight sections of the linear macromolecules which makes them ideal for LAM investigation. After a long search Prof. W. L. Peticolas in Eugene, Oregon, was willing to accept my coworker H. G. Olf to find out with his instrumentation whether the annealed oriented single crystal mats of PE obtained from a dilute xylene solution yield the expected LAM scattering. They succeeded⁵, with the just then applied iodine vapor filter, in reducing the intensity of the primary light. But in spite of the chain parallelism with the orientation of the probe one could not clearly decide whether D , the thickness of the crystalline core, or L , the easily measured small angle X ray scattering long period, determines the observed Raman frequency shift ν' .⁶ Both increase with the temperature of annealing, while ν' decreases as expected from the increased length of the oscillating rods by which one may characterize the straight sections of the macromolecules. Raman observably the rods oscillate with a fixed center which excludes the second, fourth, sixth, and higher orders, and have nearly maximum amplitudes at the ends. In the ideal case with the maximum amplitude exactly at the ends, the ratio of their frequencies to the basic frequency is 3, 5, 7, and so on. Actually one observes slightly lower values down to 2, 4, 6, and so on, respectively, which indicate on the oscillating rod a more internal position of the maximum amplitude.

The interest in proper explanation of LAM spectra and in coordination of the frequency shift with lamellar crystalline core thickness D or the long period L became more urgent after the recent application of LAM spectroscopy to prove the identity of single crystals of PE obtained from dilute solution and from the melt.⁷ Since the experiments were performed or extrapolated to the same supercooling and temperature, one may expect that the initial amorphicity l/L at any temperature did not change with time although l is definitely larger in melt crystallized samples than in crystals from very dilute solution.⁸ Hence the claimed identity of L means also an identity of D . The reason for such a statement is that, according to the here presented model with finite viscoelasticity of the amorphous layers, their thickness $l/2$ on each side of the folded chain lamella does not substantially change L_R as long as its oscillation attenuation length l_d is sufficiently smaller than $l/2$. The identity of the observed frequency shift in both cases means an identical D although the authors have done their best to prove the identity of L which does not apply too well.

The possibility of measurement of the straight section between the crystal defects, or the crystal defect and the surface transition of the chain from crystalline to amorphous conformation, or between two such transitions is in some respect similar to the initial analysis of randomly coiled macromolecules in the melt or solution by Schimanouchi et al.¹ The difference is in the connecting sections of the macromolecule. They are well defined in the case of Schimanouchi who investigated dilute solutions where the dissolved molecules are completely independent of one another. In the case of crystals, however, the oscillation in the amorphous region does not remain on the same molecule but jumps from one molecule to the other to reach

in the end the other side of the interruption. If the oscillations do not influence each other, one may obtain from the spectrum of scattering intensity a true picture of the distribution of the length of oscillating sections, whether they are created by the interruption in the surface layers of the lamellae or by crystal defects.

Oscillating Rod Model (Continuous System)

In order to treat the LAM oscillating straight molecular sections one replaces them with an elastic rod which is either completely free, or is embedded in, or continued by, elastic amorphous material or has additional forces at the ends. The same treatment has to be applied to the neutron spectrum of the lowest eigenvalues of standing waves in the sample⁹ since they are mainly determined by LAM oscillations, irrespectively of their observability by Raman scattering.

This replacement may be relatively easily applied to PE, which in the straight sections has an uninterrupted sequence of trans conformations. One must be a little more cautious in polytetrafluoroethylene, polyoxymethylene, poly(ethylene oxide), isotactic polypropylene and polystyrene, where the crystals contain only regular helices so that the amorphous phase differs from the crystals solely in the irregularity of sequences of gauche and trans conformations. In all cases the problem is one-dimensional since the influence of the lateral van der Waals forces which are much lower than the covalent longitudinal forces may be completely neglected¹⁰ and the helices are treated as straight chain sections parallel to the helical axis.

The noncrystalline layers or the crystalline defects are entered from the straight sections of the fully extended crystallized chains by the LAM oscillation at the point where the regular sequence of conformations is interrupted either by the end of the central crystalline core of the lamella or by the defects or chain ends inside the core. In the first case, the observed L_R is slightly smaller than D and not close to L , which seems to play no role at all. In the second case, LAM oscillating straight section L_R is always smaller than the straight section of the macromolecule between two defects or between the surface and the defect, which in both the latter cases is smaller than D .

Physically, the situation is rather simple. The straight sections of the macromolecule are in crystal arrangement of average thickness D if the chains are perpendicular to the lamellar surface while the long period L is the average sum of the thicknesses of the crystalline lamella D and the separating amorphous layer l .

$$L = D + l \quad (1)$$

In the latter component, the macromolecule has a random conformation which cannot oscillate over half the thickness of the amorphous layer, $l/2$, like a both side linear expansion of the highly elastic accordion of length D to yield as length of the oscillating rod $L = L_R$. In such an extreme, rather unrealistic case, the ends are oscillating in the opposite direction and hence demand a strong repulsive force at $\pm l/2$ from the center of the rods.

The observed LAM frequency shift in wave numbers per unit length, $\nu' = (E_c/\rho_c)^{0.5}/2cL_R$, and the hence deduced $L_R = \lambda_c/2 = D'$ corresponds more to D than to L . Here c is the velocity of light in vacuum, E_c the elastic modulus of the straight section, i. e., of the crystal in chain direction, and ρ_c the assumed uniform density of the crystal. The question remains how the amorphous conformations of the chain influence the LAM oscillation of the crystallized straight sections and whether they really oscillate independently.

The simplest solution was to consider uniquely the straight crystalline rods which are fixed in the center, have the maximum amplitude at the ends, an elastic modulus E_c , and density ρ_c in exactly the same way as it was formerly done with fully stretched crystalline paraffin molecules (independent oscillators). Since this was not sufficient to explain the rapidly expanding experiments¹¹⁻¹³ the amorphous layers were included as an infinite medium in which the oscillating straight sections were immersed.¹⁴ One went still further and assumed a finite thickness of amorphous layers and considered the oscillation of a one-dimensional channel containing alternate crystalline and amorphous sections. But in all calculations it has always been assumed that the rods and the amorphous sections between them do not vary at all. In such a case the solutions of a single rod can be extended to all the sequences because the averages are identical with the values of a single rod with its amorphous environment.

If the only differences between the crystalline and amorphous layers are in the elastic modulus E and density ρ , then one observes, with increasing volume amorphicity, $1-\sigma_v$, and ratio of the oscillation resistances, $(E_0)^{1/2}$ of the crystalline and amorphous layers, a gradual shift of oscillation energy to the layer of smaller resistance.¹⁵ The finally prevailing oscillation amplitude of the amorphous layers starts to dominate so completely the oscillations that from the observed shift ν' one is unable to reach any decision on the thickness of the straight sections if they vary in longitudinal direction. As shown in Figure 1, the predominance of the purely elastic amorphous layers couples the rods and distorts even the basic oscillation of a sequence of unequal rods so much that there is no possibility of an analysis of the single rod lengths. One obtains an average over all cooperating straight sections which changes with higher eigenvalues so that, at least in principle, one may try to deduce from them the distribution and length of the cooperating straight sections. According to these theoretical models the observed LAM spectrum normally obtained with the basic eigenvalue cannot be decomposed in contributions from single straight sections. The interaction between the straight sections connected by amorphous conformations yields averages over the former without detailed information on them. This is in perfect disagreement with experiments.

Secondly, the chains either remain in the same crystal which is the only possibility in crystals from dilute solution (below 0.01%) or may go to some adjacent crystal, as it happens at higher solution concentration, in crystallization from melt, and during annealing of oriented mats of completely separated PE single crystals as obtained from a dilute solution.¹⁶ In the former case one obtains a thin and in the latter case a thick amorphous layer separating the crystalline cores.^{17,18} In both cases it is difficult to choose in the

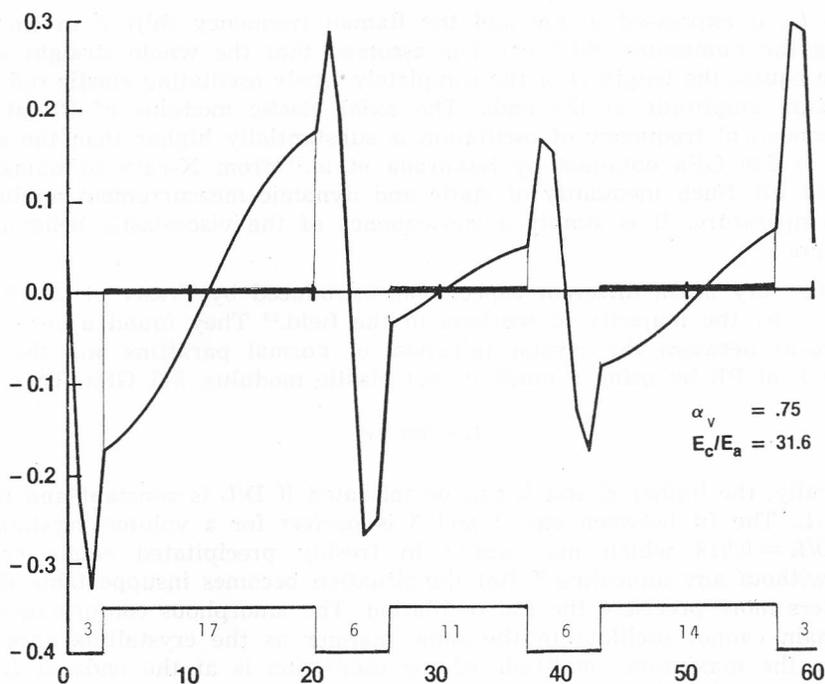


Figure 1. Mutual interference of LAM oscillations of three unequal rods, 17, 11, 14 long, separated in the longitudinal direction by purely elastic amorphous layers of equal thickness 6. The Raman frequency shift ν' is proportional to the average length of the three rods and does not split at all in a triplet characteristic of three different rods. The whole sample is a regular repetition of the three rods.

continuous model the proper direction of the chain or of the channel by which the oscillation is transferred from one crystal to the next. The situation does not improve by considering in more detail the oscillation modes of the chain which contains an interruption of straight conformations at crystal defects or passes the frontier between the crystalline and amorphous layers.

Chains with Forces at the Ends

In monodisperse paraffin single crystals, each layer corresponds to the length of the paraffin chain. In such a case the single oscillating chain is indeed representative of the whole system of parallel crystals. Each chain has at both ends a CH_3 group. It repels a similar group on the former or the continuing molecule which oscillates in the opposite direction with a stronger force than that between the usual CH_2 groups oscillating in the same direction with a marginal difference in amplitude. As calculated by Krimm et al.¹⁹ such an additional force increases the basic frequency shift ν' . If one takes it explicitly in account, one may calculate the elastic modulus of the straight PE chain as 290 KPa²⁰ yielding

$$L_R = 283.8/\nu' \quad (2)$$

where L_R is expressed in nm and the Raman frequency shift ν' in cm^{-1} . In finding the numerator 283.7 one has assumed that the whole straight chain section equals the length D of the completely freely oscillating elastic rod with maximum amplitude at the ends. The axial elastic modulus of PE at this high acoustical frequency of oscillation is substantially higher than the static value of 240 GPa obtained by Sakurada et al.²¹ from X-rays of uniaxially strained PE. Such inequality of static and dynamic measurement applies to any temperature. It is simply a consequence of the viscoelastic behavior of polymers.

One very much different aspect was introduced by Fraser et al.^{22,23} and followed by the majority of workers in the field.²⁴ They found a very good agreement between the crystal thickness of normal paraffins and the long period L of PE by using a much higher elastic modulus, 341 GPa. They proposed

$$L = 309.3/\nu' \quad (3)$$

Physically, the higher E and L can be tolerated if D/L is constant and hence also $1/L$. The fit between eqs. 2 and 3 is perfect for a volume crystallinity $\alpha_v = D/L = 0.918$ which may apply to freshly precipitated single crystal mats without any annealing.¹⁶ But the situation becomes insupportable if one considers more precisely the rod oscillation. The amorphous conformations of the chain cannot oscillate in the same manner as the crystalline ones. Secondly, the maximum amplitude of the oscillation is at the ends of L and there reverses its direction if one goes from one crystal to the next or previous one. Hence, as in paraffin crystals, one expects a strong compressive force from the touching ends of the rods oscillating in opposite direction, resulting in higher frequency of oscillation. This was never observed or reported. Moreover, it is obvious that in such a case the oscillations of the straight sections of the subsequent crystals are not independent any more. The LAM frequency corresponds to the average of chain lengths of all cooperating sections so that the packing of the crystals becomes more important than the variation of straight chain length in a single crystal. One obtains information on the former fact and misses any information about the distribution of lengths.

The group of I. M. Ward in Leeds, U. k., has found that rather generally L_R of PE is smaller than L and nearly identical with the crystal thickness D as determined by other independent methods.^{24,25} They use $E_c = 340$ GPa, i. e., eq. 3 which is supposed to yield L and not the smaller D . Their findings agree with the here later introduced viscoelasticity of the amorphous areas where L_R is slightly smaller than D .

Damped Oscillations in the Viscoelastic Amorphous Layer

A straightforward solution is found by a closer consideration of the oscillation of the straight section of the linear chain. As soon as the sequence of trans conformations in PE is interrupted by a gauche conformation, the LAM oscillation has either the possibility to remain on the same chain²⁶ which changes direction or to jump to some properly located adjacent chain.²⁷ This second possibility whose probability in PE increases with the number of

closely adjacent gauche conformations always occurs in concentrated solutions which are similar to the melt and to chains in amorphous layers and crystal defects. Each change of the direction of oscillation and each jump to another molecule irreversibly transforms a fraction of the oscillating energy into heat, as described by the viscous component of the viscoelastic modulus of the sample.

The situation seems rather similar with polymers which in crystals assume helical conformations. The axis of the helix determines the longitudinal direction of the oscillating rod. As soon as this direction changes one is faced with the same problem as in the case where the direction of the PE molecule changes. The longitudinal oscillation may remain on the same macromolecule which changes direction or it may jump onto a closeby macromolecule with minor or no change in direction.

For a viscoelastic medium with the complex elastic modulus $E^* = E' + iE''$ one has the complex velocity of sound $v^* = v' + iv''$ with $v' = \{[E' + (E'^2 + E''^2)^{1/2}]/2\rho\}^{1/2} = \{[(\rho)^{1/2} - E']/2\rho\}^{1/2}$ [the abbreviation $(\rho)^{1/2} = E'^2 + E''^2$] and $v'' = \{[(\rho)^{1/2} - E']/2\rho\}^{1/2}$. The wave length λ^* is proportional to the velocity, $\lambda^* = \nu v^*$. The frequency of oscillation is ν . In $2\pi i/\lambda^*$ one has the complex quantities $1/\lambda^* = (1/\lambda_a^*)' - i(1/\lambda_a^*)''$ with $(1/\lambda_a^*)' = \nu \{\rho [(\rho)^{1/2} + E']/2\}^{1/2}/(\rho)^{1/2}$ and $(1/\lambda_a^*)'' = \nu \{\rho [(\rho)^{1/2} - E']/2\}^{1/2}/(\rho)^{1/2}$.

The oscillating amplitude of the amorphous component of the sample falls from the boundary between the crystalline and amorphous component at $D/2$ as $\exp[-\{x - D/2\}/l_d]$. It is zero at the center of the layer, $x = L/2$. This requires in the amplitude a factor $-\sin[2\pi(L/2 - x)(1/\lambda_a^*)']$, leading to the usual formulation of the amplitude $\xi(x)$ of a damped oscillation

$$\begin{aligned} \xi_a &= -A_a \sin[2\pi(1/\lambda_a^*)'(L/2 - x)] \exp[-2\pi(1/\lambda_a^*)''(x - D/2)] = \\ &= -A_a \sin[2\pi(1/\lambda_a^*)'(L/2 - x)] \exp[-(x - D/2)/l_d] \end{aligned} \quad (3)$$

The attenuation to $1/e$ of the initial amplitude occurs over damping distance $l_d = (1/2\pi)(1/\lambda_a^*)'' = (1/2\pi)(\rho)^{1/2}/\{\rho[(\rho)^{1/2} - E']/2\}^{1/2} = (1/2\pi)(\rho)^{1/2} + E'/E''/(1/\lambda_a^*)'$ which may be smaller than $l/2$, the thickness of half the amorphous layer. The last expression for the damping length gives it as multiple of the oscillation wave length in the amorphous component, $(1/\lambda_a^*)'$. The factor 2 makes at $E''/E' > 0.3266$ the damping length nearly equal to, or smaller than, λ_a .

At the transition point from the crystal lattice to the amorphous layer the boundary conditions demand the equality of the amplitude $\xi(D/2)$

$$A_c \sin \pi D/\lambda_c = A_a^* \sin [\pi(L - D)/\lambda_a^*] \quad (4)$$

and of the mechanical stress $Ed \xi/dx$

$$A_c E_c (2\pi/\lambda_c) \cos(\pi D/\lambda_c) = -A_a^* E_a^* (2\pi/\lambda_a^*) \cos[\pi(L - D)/\lambda_a^*] \quad (5)$$

in both media if $D/2$ and $(L - D)/2 = l/2$ are the distances from the fixed centers of the crystalline and amorphous layer. Since the first condition, eq. 4, yields a real amplitude the second condition, eq. 5, can be rewritten so that one obtains at the boundary

$$A_c E_c / \lambda_c \cos(\pi D / \lambda_c) = -A_a \{ E_a' (1 / \lambda_a^*)' \cos[\pi(L - D)(1 / \lambda_a^*)] + E'' (1 / \lambda_a^*)'' \sin[\pi(L - D)(1 / \lambda_a^*)] \} \quad (6)$$

No consideration is made of the existence and finite width of the certainly existing transition layer between both components where the chains still remember their parallelity in crystal lattice and hence do not assume complete randomness of orientation as required in a truly amorphous material. In our treatment the transition from the crystalline to perfectly amorphous area is abrupt without any transition layer.

In order to satisfy the boundary conditions one has to solve the equation

$$\tan[(\pi/2)y] = -u' \tan[(\pi/2)z''y] / \{1 + (u'/u'') \tan[(\pi/2)z'y]\} \quad (7)$$

with

$$y = D/D' = D/L_R = 2D/\lambda_c \quad (8)$$

$$u' = (E_c \rho_c / E_a' \rho_a)^{1/2}$$

$$u'' = (E_c \rho_c / E_a'' \rho_a)^{1/2}$$

$$z' = [(L - D)/D] (E_c \rho_a / E_a' \rho_c)^{1/2} = (1/\alpha_v - 1) (\rho_a / \rho_c) u'$$

$$z'' = [(L - D)/D] (E_c \rho_a / E_a'' \rho_c)^{1/2} = (1/\alpha_v - 1) (\rho_a / \rho_c) u''$$

The right side of eq. 7 contains three parameters u' , u'' , and $\zeta = (1/\alpha_v - 1) \cdot (\rho_a/\rho_c)$ with $z' = \zeta * u'$ and $z'' = \zeta * u''$. If $y = D/D' = D/L_R = 2D/\lambda_c$ is larger than 1, which happens with z' smaller or close to z'' , the straight section oscillates with $\lambda_c < 2D$. The maximum of oscillation is inside and not at the ends or even in the continuation of the rod. The situation gets reversed if $y < 1$ yielding $L_R > D$.

At the measured E' and E'' of the viscoelastic response of such samples the ratio z'/z'' with increasing thickness l of the amorphous layer (increased amorphicity $\alpha_v - 1$) very soon jumps over the limit so that one expects $D' > D$. The oscillating rod seems to longitudinally expand in the amorphous layer; the oscillating rod is longer than the straight section of the chain. The maximum of the LAM amplitude of the rods is outside the rod. At the boundary between the crystals and the amorphous layer the oscillation amplitude and the mechanical stress in the crystal increase with increasing x . The boundary condition, eq. 6, requires a greater increase of the amplitude and gradient in the weaker amorphous component in order to yield, in spite of the so much smaller elastic modulus, the equality of stress. As a consequence, one has a strong oscillation in the amorphous layers as soon as the maximum of oscillation is outside the rod, i. e., $y < 1$. If the damping is not strong enough, there is a substantial longitudinal coupling of straight chain sections in the sample. With decreasing ratio $u'/u'' = (E_a''/E_a')^{1/2}$ the limit between easily explainable and hence called reasonable $y > 1$, which never yield exaggerated amplitudes in the amorphous areas, and the irrational $y < 1$, where the amplitudes may rise beyond those in the crystalline areas, is shifted to smaller z ratio. The limit 1 for $z = 1$ is reached with $u'/u'' = 0$, i. e. for $E_a'' = 0$ (Figure 2). At higher z the limit moves to higher viscous component given by the higher $u'/u'' = E_a''/E_a'$.

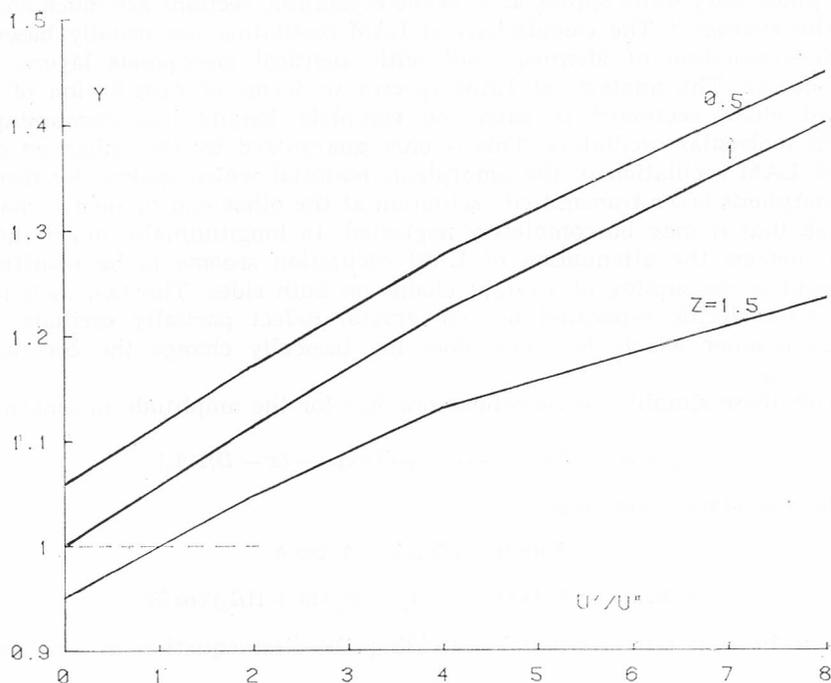


Figure 2. $y = D/D'$ for $z = 0.5, 1$ and 1.5 as function of $u'/u'' = (E_a''/E_a')^{1/2}$. $y = 1$ corresponds to $u'/u'' = -1/\tan[(\pi/2)z] = -1, 0, +1$.

Increased Damping in the Amorphous Areas and Crystal Defects

In spite of the damping the smallness of $E_a \ll E_c$ (E_a means E' or E'' of the amorphous layer) causes the amplitude in the amorphous layers to be, at least at small distances from the transition from crystalline to amorphous conformation, $x - D/2$, higher than that in the crystalline core. It may happen that the oscillation energy of amorphous layers becomes dominant so that the observed LAM frequency shift and amplitude is gradually almost completely independent of the individual length of the straight sections of crystallized parts of the macromolecule. In such a case, the transfer of oscillating energy through the amorphous layer is still quite large so that the longitudinal decoupling does not occur or is not sufficient. Since eqs. 5, 6, 7 are based on zero amplitude in the center of the amorphous layer, as caused by the oscillating factor, they are not concerned with the decoupling of the LAM oscillations in rods of adjacent lamellae which depends on the absolute value and the decay factor of oscillations in the connecting non-crystalline layer. The assumed longitudinal decoupling of LAM oscillation requires a rapid attenuation in the amorphous layer so that the amplitude practically completely disappears before reaching the opposite side of the layer. The value of the amplitude in or close to the center of the amorphous layer must be small enough to assume its practical disappearance at the other end of the layer.

Actually, even in a strictly longitudinal channel with lateral dimensions of a single macromolecule, the lengths D of the crystalline and l of the amor-

phous phase vary quite appreciably. Some crystalline sections are much shorter than the average.¹⁰ The calculations of LAM oscillation are usually based on regular alternation of identical rods with identical amorphous layers. This never occurs. The analysis of LAM spectra in terms of distribution of crystallized chain sections²⁶ is based on complete longitudinal decoupling of straight molecular oscillators. This is only guaranteed by the enhanced damping of LAM oscillation in the amorphous material which makes the through the amorphous layer transmitted oscillation at the other end of such a channel so weak that it may be completely neglected. In longitudinally much shorter crystal defects the attenuation of LAM oscillation seems to be insufficient for complete decoupling of straight chains on both sides. The two sections of the macromolecule separated by one crystal defect partially oscillate in a coupled manner which, however, does not basically change the conclusions about them.

With these simplifying conditions one has for the amplitude in amorphous layer

$$\xi_a = A_a \cos [k_a (x - D/2) + \delta] \exp [-(x - D/2)/l_d] \quad (9)$$

and the boundary conditions

$$\begin{aligned} A \sin [(\pi/2) D/D'] &= A_a \cos \delta \\ k_c E_c \cos [(\pi/2) D/D'] &= -A_a [k_a E_a \sin + (1/l_d) \cos \delta] \end{aligned} \quad (10)$$

Equation 10 may be rewritten by dividing the first equation by the second one

$$\tan [(\pi/2) y] = -u (\pi/2) y / [1 + k_a l_d \tan \delta] \quad (11)$$

with

$$u = (E_c/E_a) (2 l_d/D)$$

In the pure viscoelastic case one has chosen δ in such a way that the amplitude of oscillation vanishes in the center of the amorphous layer (eqs. 4—7). But since the structure is not uniform with identical L or D or l , the center of the amorphous layer is not a similar singular point as the center of the crystalline core where the LAM oscillating rod or straight section of the macromolecule is fixed. The longitudinal decoupling between the rods is only assured if the oscillation in the amorphous layer decreases enough at l after the whole amorphous layer is traversed. This means that $\xi (L/2 + 1)$ is smaller than $\xi (D/2)/10$. For this one has to assume $l = 2.3 l_d$. The same consideration has to be applied to crystal defects which have to be longitudinally longer than $2.3 l_d$. Since this is a rather exceptional length of a crystal defect one has through it some coupling of the longitudinal oscillations of straight chains on both sides. This partial coupling is usually so weak that it does not severely affect the observed Raman spectrum because the cooperating straight sections with the intervening defects are together smaller than the thickness of the crystalline core of the lamella. In such a case the average over the coupled oscillators is not very different from the length average of the oscillators that roughly centers about half the crystal core thickness D if there is one defect per passage.

In Ref. 28 one simply assumed $\delta = 0$ and hence obtained the solutions of eq. 11 which now reads

$$\tan [(\pi/2) y] = -u (\pi/2) y \quad (12)$$

from the intersections of both systems of curves representing the left and right side of eq. 12, as shown in Figure 3. A more sophisticated approach may

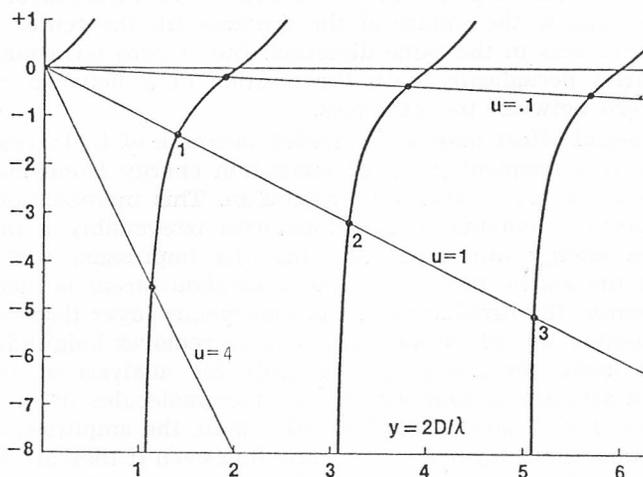


Figure 3. The left and the right sides of eq. 12 for $u = (E_c/E_a) (2l_d/D) = 0.1, 1$ and 4 .

find a better value for δ which is still open. The value $\delta = 0$ determines the initial slope in the amorphous layer by the inverse decay length $1/l_d$. A small positive δ accentuates the decrease of the amplitude in the amorphous layers by the contribution of the periodic term. It also reduces the inclination of the straight lines representing the right side of eq. 11. With approaching $\pi/2$ the straight lines are horizontal through the origin yielding as intersections $y_n = 2n$. In this case the rods seem to oscillate with fixed ends which does not yield any Raman scattering. Since in any undeformed semicrystalline sample the LAM corresponding Raman scattering was observed, this extreme case may be excluded as unrealistic.

In order to fulfill the boundary conditions at the transition from the purely elastic crystalline to the viscoelastic amorphous layer on the broad surfaces of the thin lamella one has the maximum amplitude of LAM oscillation a little before the ends of the crystalline rods, L_R is slightly smaller than D . In such a case the amplitude in the amorphous layer is always smaller than in the crystals so that it hardly plays a role even in high crystallinity samples. The difference in the wave length between D and $L_R = \lambda_c/2$ is extremely small in a situation which is close to that in PE (Figure 2). It remains very little dependent on the decay length l_d of the amorphous component if this is sufficiently smaller than the layer thickness.

The amplitude in the center of the amorphous layer is by the factor B reduced amplitude at the beginning of the layer, i. e., at the boundary between the crystal core and the amorphous layer

$$A_a \cos [(\pi/2) y (1/D) (E_c \rho_a/E_a \rho_c)^{1/2}] \exp [-(l/2 l_d)] = (A_a \cos \delta) B \quad (13)$$

with

$$B = \{ \cos [(\pi/2) y (1/D) (E_c \rho_a/E_a \rho_c)^{1/2}] / \cos \delta \} \exp [-(l/2 l_d)]$$

If $l \gg 2l_d$, the exponential factor makes the amplitude in the center, $\sim B$, and at the other end, $\sim B^2$, of the amorphous layer so small that no longitudinal coupling of oscillating rods may occur. After the whole layer is traversed, the amplitude falls to the square of the decrease till the center of the layer. The phase factor acts in the same direction. But it does not count very much because it varies periodically with the position of x between $+1$ and -1 and crosses zero between the extremes.

A very special effect makes the needed decrease of l_d . In real amorphous systems there is a frequent jump of oscillation energy from one bent molecule to the next in more favorable orientation. This increases quite substantially the observed damping which transforms irreversibly a larger part of the oscillation energy into heat. One has the impression that the viscous component of the elastic modulus of the amorphous areas is much enhanced. As a consequence, the oscillation in the amorphous layer decreases fast and, thus, after crossing the whole amorphous layer removes longitudinal coupling which would make the LAM spectra unfit for analysis of the fractional distribution of straight section lengths of macromolecules in the sample.

As soon as $D' < D$ and l_d is sufficiently small, the amplitudes of the oscillation in the amorphous layer are so minute that even if they are Raman active they hardly contribute to the observed LAM spectrum of the sample. Hence one has to pay very little attention to LAM oscillations in the amorphous layers as soon as they are sufficiently attenuated.

The introduction of viscoelasticity and the enhancement of its viscous part is particularly needed if one compares the frequency of the observed higher harmonics or the ratio of their frequency with that of the basic oscillation. This ratio seems to be always between 2 and 3, 4 and 5, 6 and 7, and so on, as it occurs as soon as the maximum amplitude is not at the ends of the oscillator but a little earlier. The calculations were made for the case where all rods are equal and the amorphous layers between the parallel rods containing lamellae are perfectly smooth and of equal thickness. If the sample is polydisperse, as it always is, and the oscillations are completely free, one has to add in the spectrum the ν' of the components with an intensity proportional to the fraction of such chains. If $\delta = 0$, one obtains $y_2 = 3y_1$, $y_3 = 5y_1$ and so on as it corresponds to completely free oscillations of rods in the case of $E_c l_d / E_a D = \infty$ having the maximum amplitude at the ends of the rods (Figure 4). Such a case may be established by $E_a = 0$, i. e., by not having, in the layer separating the rods, any material so that the rods can oscillate completely freely without any connection with those in the neighboring crystals. The opposite extreme happens with $E_c l_d / E_a D = 0$ corresponding to the oscillation of rods fixed at the ends (no Raman scattering). In this case the amorphous layer is completely rigid, $E_a = \infty \gg E_c$.

Complete decoupling of oscillation of the longitudinal, following the straight polymer section is only possible if l_d is substantially smaller than the longitudinal extension of the amorphous layer or the crystalline defect. The last condition demands that l_d is not much longer than the persistent length²⁹ of the macromolecule in melt or in solution, i. e., 2 or 3 links in the case of LPE. In such a length, the LAM oscillation has enough probability of jumping to the properly oriented adjacent macromolecule instead of changing direction and thus remaining on the same but bent macromolecule. Hence, for $D = 200 \text{ \AA}$ a ratio $l_d/D = 1/30$ to $1/50$ has to be inserted in eqs. 9–11 and 13.

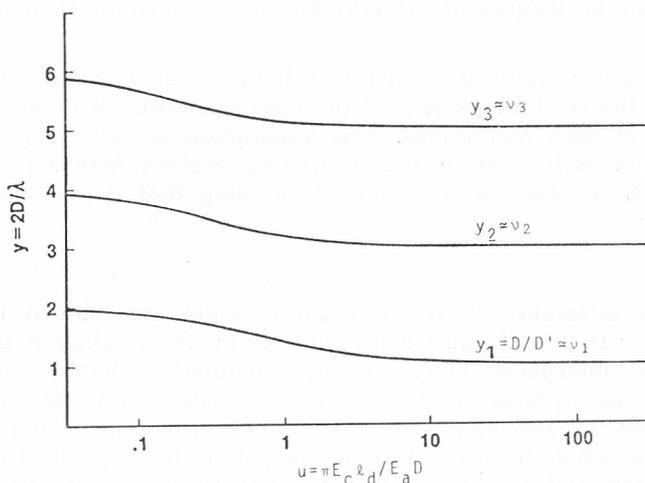


Figure 4. The Raman frequency shift $\nu_i' \sim y$ of higher harmonics of LAM oscillation as function of the attenuation, l_d , and elasticity, E_a , of the amorphous layer. They go from 2, 4, 6 ν_1 to 1, 3, 5 ν_1 corresponding to perfectly individual rods without any coupling fixed at the ends to rods fixed at the center.

If l_d is larger, the longitudinal dimensions of a great many crystal defects are not sufficient for complete decoupling. The two straight sections of the crystallized macromolecule separated by the crystal defect do not oscillate quite independently as supposed in the analysis of their spectra.³⁰ One, hence, observes not only the independent oscillations of the new straight sections into which D is split by the crystal defect but also their partial superposition. This makes the precise analysis of the observed spectrum a little more complicated although it does not basically change the issue. Even with complete coupling one has a Raman frequency shift which is proportional to the inverse average of the two sections, i. e., between $D/2$ and ∞ . The upper limit is so faintly occupied that one may forget about it. The LAM spectrum has a long, increasingly weaker tail which very soon merges with the background. With partial coupling, the common frequency of both sections decreases rather fast so that nothing can be associated with it as soon as the maximum intensity in the disordered area is below 0.1 of the boundary intensity. The intensity of the oscillation is proportional to half the square of the amplitude multiplied by the elastic modulus. Even in rather short crystal defects and a much larger decay length, $l_d > l_{\text{defect}}$, the coupling is so weak that the coupled oscillation makes only a small proportion of the actual independent oscillation of the two sections. A spread in crystal defects may be monitored by the width of the corresponding LAM spectrum without any substantial interference by the certainly existing coupled oscillations of the sections which are not sufficiently separated by the longitudinally too short defects. A similar consideration may be made for two or more defects on the same originally straight section of the macromolecule extending from one to the other flat surface of the lamella. But remember that such an optimistic analysis is only possible if the LAM oscillation in the disordered area is heavily damped. The undamped oscillation in the disordered areas provides ample coupling so that one ob-

serves averages of lengths of straight sections instead of their independent oscillations.

All the practical application of the shift in Raman frequency by the LAM oscillations of the straight sections of the macromolecules is based on complete independence of such oscillations. This assumption is only supported by the damping of the oscillation in the disordered regions between the crystals, which so much reduces the longitudinal coupling that it may be completely disregarded.

DISCUSSION

The main differences between various models are shown in Figure 5 where for $\alpha_m = D/L = 0.7$ (a), 0.8 (b), and 0.9 (c) the oscillation is undamped (purely elastic amorphous layer), strongly damped (enhanced viscous component of the amorphous layer), and the oscillating rod has the length of the long period L . The amplitudes are shown from one center of the rod to the next, the whole length is L . The strong lines correspond to the situation in crystals ($D/2$) and the weak lines to that in amorphous layers (l). The oscillations in the left crystal are extrapolated (broken lines) to the next intersection with the horizontal line, $l = 0$, in order to show the observed L_R . In the first case, the oscillation of the amorphous layer starts to dominate with increasing amorphicity $1 - \alpha_m$ so that in subsequent harmonics one observes different averages of all cooperating straight sections, as shown for the basic oscillation in Figure 1. This effect is not shown in Figure 5 since the lengths of all the rods and amorphous layers in the sample are assumed to be equal to those in the figure. In the second case, the damping in the viscosity enhanced viscoelasticity decouples, at least at crystallinity 0.7 and 0.8, perfectly the oscillation of the molecular rods which are situated in longitudinal continuation of one another but located in the neighboring lamellae. At crystallinity 0.9 this is not completely true because the intensity of oscillation does not decrease sufficiently till the center of the amorphous layer. The decrease from the center to the other boundary of the layer is not included. The drop in oscillating amplitude in the center at $x = L/2$ is the consequence of plotting, which shows the initial decrease between the outer boundary and the center of the amorphous layer of the oscillating amplitude connected with the amplitude of the crystalline phase. The total amplitude decrease is so strong that the transmitted amplitude is less than $1/5$ of the entering amplitude and hence, even in this extreme case, the coupling nearly negligible. In the third case, the oscillation of the rods of length L demands the same crystalline mechanical properties, i. e., the very high elastic moduli in the amorphous layers, and enormously increases the LAM frequency by the strong forces caused by the opposite direction of oscillation of the touching ends. One end of the horizontally positioned rod oscillates to the right and the adjacent end of the next rod to the left.

In contrast to the usual treatment of purely elastic and even normal viscoelastic amorphous layers with gradual transfer of the oscillation energy density to the amorphous regions, the enhanced viscosity of the amorphous material makes the oscillation decay so rapid in these layers that the transfer of oscillation to the next crystal or continuation of the straight section of the chain becomes negligible. Since lateral neighbors hardly affect the chain

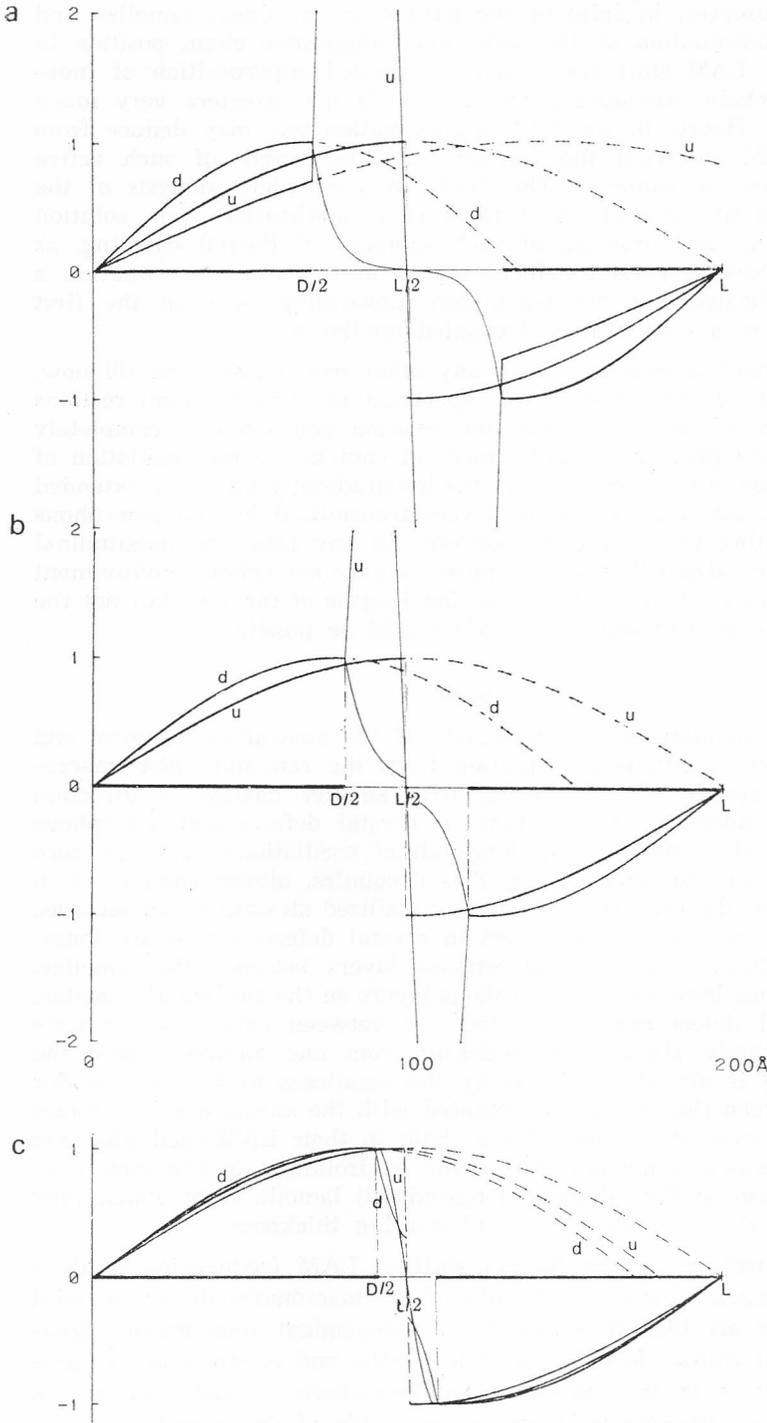


Figure 5. Amplitude distribution of LAM oscillation between the two subsequent centers of the identical oscillating rods in the area of straight (crystals) and randomly coiled (amorphous layers) conformations for crystallinity (a) 0.7, (b) 0.8, and (c) 0.9. One has assumed $E_c/E_a = 100$, $\rho_c/\rho_a = 1.174$, $\nu_c/\nu_a = 10.83$. The heavy lines represent the oscillation amplitude of the crystalline component due to (d) the enhanced viscous component of the viscoelasticity of the amorphous layer with the damping length $l_d = 0.08L \ll \lambda_a$ and $L_R < D$, (u) the undamped purely elastic amorphous layer with $L_R > D$, and the extension of the elastic rod oscillation over the whole long period with $L_R = L$ where the adjacent ends oscillate in opposite direction and the amorphous layers behave as crystals. The weak lines represent oscillations in the amorphous layer of the monodisperse system. The broken lines are continuation of the first part of the full lines yielding $L_R = \lambda_c/2$. The weak lines of the damped case are calculated to the center of the amorphous layer where they show a discontinuous step to the line of damped oscillation in the other half of the amorphous layer coming from the next oscillator.

oscillation⁸ one observes, in spite of the parallelism of linear lamellae and the long range continuation of the same crystallographic chain position in the lattice in the LAM shift the nearly unimpeded superposition of independent straight chain oscillations. The chains do not interfere very much with one another. Hence, in the first approximation one may deduce from the observed LAM spectrum the fraction and the length of such active straight sections in the sample.²⁶ This leads to a complete analysis of the roughness of lamellar structure as formed in crystallization from solution or melt,³⁰ annealing and drawing of such samples.^{31,32} Partial coupling, as it most likely occurs in crystal defects, makes in this case the situation a little more complicated but not completely unsolvable since in the first approximation there are still fairly decoupled oscillations.

Such a treatment is impossible with any other model presented till now. The usual practice of derivation of the spectrum of straight chain sections from the spectrum of observed LAM line position and shape is completely unsupported by any previous theory which, in contrast to the oscillation of completely free rods in the vacuum or in the longitudinally infinitely extended amorphous region, also considered the forces transmitted by the amorphous component separating the crystalline sections. In any case, the longitudinal coupling of rod oscillations through the purely elastic amorphous environment is so strong that only averages of the varying lengths of the rods but not the distribution and lengths of individual rods would be possible.

CONCLUSION

The enhanced damping by viscoelasticity of the amorphous material and by the jumping of longitudinal oscillation from the randomly bent macromolecule to the closeby macromolecule with smaller change of direction produces a rapid decrease of amplitude in crystal defects and amorphous layers separating the crystals. The longitudinal oscillations approach zero long before they traverse such layers. This decouples, almost completely in the chain direction, the oscillations of the crystallized straight chain sections. The decoupling seems to be less perfect in crystal defects which are longitudinally much thinner than the amorphous layers between the lamellae. Hence, these sections between the amorphous layers on the surface of lamellae, between a crystal defect and one surface, or between two crystal defects oscillate longitudinally almost independently from one another. Since the lateral decoupling is already achieved by the smallness of lateral van der Waals forces between the chains, as compared with the strong covalent forces in the chain, the straight sections of the chain in their LAM oscillation are indeed nearly completely independent of the environment in the same crystalline (lateral) and in the adjacent (longitudinal) lamella from which they are separated by the amorphous layer of varying thickness.

Hence, the spectrum of the Raman shift of LAM frequencies yields a distribution of lengths of straight sections of the macromolecule in the solid investigated. They act like an assembly of independent rods whose eigenfrequencies are, of course, modified a little by the end groups and the properties of the chains in the amorphous conformations, partially in defects and partially in the amorphous layers on each side of the lamella.

The situation is completely different in the case where only elastic properties of the amorphous conformation without the viscous component are considered. In the treatment of a single molecule, which is partially in the crystalline and partially in amorphous conformation, one finds more and more oscillation energy in the amorphous parts which hence couple so enormously the oscillations of the crystalline parts that with different harmonics only different averages over all straight sections of the macromolecule are observable. But the single contributions of individual rods of different length are completely hidden by the averages. The same applies to the continuous treatment of a narrow straight channel containing crystalline rods alternating with amorphous material which, besides the deficiencies of the single macromolecule, suffers from the fact that the straightforward continuation in the next crystal will almost certainly be performed by some other molecule and only exceptionally by the same one. Hence, the oscillation of the channel is not identical with that of the single macromolecule. The situation is a little more favorable in crystal defects, where the chances for continuation by the same macromolecule are much higher. But again they drop to zero at chain ends, where the continuation must be by another macromolecule.

The comparison of single crystals from solution and from the melt is only partially affected by the enhanced viscosity treatment of the LAM oscillation of the amorphous component. One may accept that the identity of LAM peaks in both cases means the identity of the thickness of the crystalline core of both types of crystals. That they certainly differ in the thickness of the amorphous surface layers of lamellae may be derived from special investigation^{8,17} although one does not know exactly the influence of the thickness growth with time which at the low temperature of crystallization from solution was not mentioned earlier. It may very much change the surface layers, as seen from the dependence of the single crystal mat density on the long period L .¹⁶ The agreement with L , the authors claim⁷, is a sign of the unavoidable low precision of the measurement of SAXS and LAM.

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SAŽETAK

Utjecaj viskoelastičnosti amorfnih slojeva na raspršenje longitudinalnog harmonikastog moda u polimerima

A. Peterlin

Normalna viskoelastičnost amorfne komponente daje brzi eksponencijalni pad amplitude longitudinalnih oscilacija »harmonikastog« tipa u defektnim područjima makromolekule u kristalnoj jezgri i u amorfnim slojevima na površinama lamele koje sadrže pregibe. Makromolekula u amorfnom sloju i u kristalnim defektima mijenja smjer i stoga ne može sačuvati longitudinalnu oscilaciju. Preskok te oscilacije na susjedne molekule toliko je brz, tako da su ravni odsječci između dva površinska sloja longitudinalno potpuno raspregnuti, dok su oni između defekta i površinskog sloja gotovo potpuno raspregnuti od ostatka uzorka. Efekt je pojačan činjenicom da je osnovna valna duljina Ramanova raspršenja manja od dvostruke duljine oscilirajućeg ravnog odsječka. Maksimum vibracijske energije pojavljuje se unutar tih odsječaka, a ne u amorfnim područjima. Budući da je bočno raspredanje osigurano bočnim silama, svaki ravni odsječak oscilira kao da je potpuno neovisan o kratkom i dugom doseg kristalne i amorfne okoline. Samo u takvom slučaju može se iz eksperimenta izvesti jednostavan zaključak o raspodjeli ravnih odsječaka lanca.