A theory of yielding of amorphous polymers at low temperature – a molecular viewpoint

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Nearly homogenous elastic shear on a molecular level rather than localized defect motion was considered to be the primary strain mechanism prior to yielding. The greatest or ideal value of the yield point for an amorphous polymer in the absence of the thermal activation was calculated. The theory involves a picture of the molecular motions under a shear stress involving three interconnected processes: 1. Shearons or intermolecular shear, 2. Rotons or intramolecular shear, 3. Tubons or motion along the covalent bond. The shear resistance was based on the stress to overcome the van der Waal's bond using a (6–12) potential. The model assumes that all atoms move co-operatively by the above motions, up to the point of yielding. Temperature was considered only as it affects the modulus, but the theory has not been extended to include thermal activation. The predicted value of shear yield point divided by shear modulus is < 0.064 to 0.092; a review of all the experimental data obtained by extrapolations to 0 K gives an average value of 0.076 ± 0.03.

1. Introduction

There are two viewpoints of shear yielding. One view considers the polymer as a viscous liquid that flows under the smallest applied stress given enough time, and the other considers the polymer as an elastic–plastic solid with a critical stress for yielding. Both viewpoints are valid depending on the temperature. At high temperatures, around T_g (glass transition temperature), the viscous viewpoint is more applicable and at the lower temperatures, the critical stress concept is better. There is an intermediate range of temperature where either or both concepts may best describe yielding.

Most theories on the yielding of amorphous polymers describe the phenomenon in continuum terms invoking concepts of free volume, springs and dashpots, and viscosity. There are some theories that take a molecular viewpoint, such as chain flexing by Robertson [1], chain twisting by Yannas and Lunn [2], chain bending via disclinations by Argon [3], a dislocation mechanism by Bowden and Raha [4], the breaking of the van der Waals' bond by Brown [5], and a co-operative model of molecular interactions by Joseph [6].

In this paper the amorphous polymer is described in terms of the average arrangement of the molecules relative to an applied shear stress. The motions of the molecules are described as the stress increases. The relationship between the stress and the intermolecular forces is calculated. Finally the maximum stress that can be sustained by the solid is calculated; this stress is the yield point. This theoretical yield stress is like the ideal yield strength that has been calculated for perfect crystals in that no defect mechanism is introduced and the contribution of thermal activation has been omitted.

Many calculations have been made of the ideal tensile and shear strength of perfect crystals. These calculations show that the ideal strength is proportional to the elastic modulus. The ratio of ideal tensile strength to Young's modulus, σ_{max}/E, and shear strength to shear modulus, Υ_{max}/G, depend on the crystal structure, and the nature of the interatomic potential. The book by Kelly [7], "Strong Solids", covers the literature on this subject.

The original calculation of the theoretical shear

stress of a crystal was by Frenkel [8] whose result is

$$\Upsilon_{max}/G = \frac{1}{2\pi} b/h \qquad (1)$$

where b is the repeat distance in the shear direction and h is the spacing of the shear planes. Kelly's review of the values of the theoretical shear stress of crystals show that they range from $\Upsilon_{max}/G = 0.24$ to 0.034. The largest ratios are for the diamond cubic structures whose interatomic bonds are directional and the smallest values are for close packed structures such as zinc and gold where central force bonding predominates.

The discrepancies between the ideal strength and the experimental values are generally attributed to defects in the crystals since differences in the methods of calculation by various investigators are relatively small. Thus surface imperfections, such as cracks, reduce the tensile strength and mobile dislocations reduce the shear strength. An ordinary zinc crystal has a yield point as low as $10^{-5}G$ whereas the theoretical strength is about $0.04G$.

Brenner [9] produced small whiskers of metals whose shear strength was near the theoretical value; for copper and silver values of Υ_{max}/G of 0.027 and 0.036 were found compared to a theoretical value of 0.039.

For amorphous polymers, a preliminary attempt [5] to calculate an ideal shear strength based on the force to separate the van der Waals' bonding using a Lennard–Jones potential gave a value of $\sigma_{max}/E = 0.037$ where σ_{max} is the yield point in tension. Yannas and Lunn [2] calculated the shear yield point of a polymer based on the twisting of a polymer chain relative to the surrounding atoms (strophons). Using a Lennard–Jones potential, Yannas and Lunn showed that $\sigma_{max}/E = 0.019$.

Bowden and Raha [4] calculated a value of the shear strength based on a dislocation model. Bowden and Raha [4] used a continuum viewpoint of the polymer. They assumed that the theoretical strength was determined by the energy to nucleate and grow a dislocation loop in an initially dislocation free material. Thus, their value of Υ_{max}/G corresponded to Frenkel's value at 0 K.

Argon [3] calculated the shear strength of an amorphous polymer based on the energy to nucleate and separate a pair of disclinations. The calculation was based on a continuum viewpoint

giving a first predicted value at 0 K of $\Upsilon_{max}/G = 0.16$ and a later value of 0.12 [10].

The Bowden and Raha model did not involve the long-chain nature of polymers. In Argon's model the yield process was based on extending an already kinked chain and thereby requiring the formation and separation of wedge disclinations. Argon did not take into account that the yield process could also involve intermolecular shear.

Isotropic amorphous polymers are often regarded as weak materials with low shear strength. However, it is remarkable, how strong an ordinary isotropic linear polymer is at low temperatures (well below T_g) when the unit of strength is Υ_{max}/G. For ordinary polymers, the value of Υ_{max}/G ranges from about 0.03 to 0.12 for temperatures below T_g. These values are comparable to the ideal strength of a face centre cubic crystal joined by a Lennard–Jones potential for which Mackenzie [11] and Tyson [12] calculated Υ_{max}/G to be 0.06.

In this paper a calculation is made of the theoretical shear strength of an amorphous linear polymer at temperatures below T_g. The polymer is viewed as a random close packed structure consisting of molecular chains bonded by a Lennard–Jones potential. The calculation is based on the general types of molecular motion that are expected under a shear stress at low temperatures.

2. Theory
2.1. Structural model
Bernal [13] has shown that an amorphous liquid consisting of spherical atoms of the same size corresponds to a random close packed structure. The average number of closest neighbours is about 11 compared to 12 for the perfect crystal. It is also observed that the density of an amorphous polymer is only about 15% different than that of the crystalline state. Both of these observations indicate that the amorphous state tends toward one of closest packing. Central force fields such as the van der Waals' bond promotes this close packing. The packing is not as close as in an amorphous aggregate of small molecules because there are restraints exerted by the strong covalent bond along the chain. The covalent bond also restricts the degrees of motion of the polymer molecule.

Since the polymer is randomly arranged, the energy of the van der Waals' bond does not have one or more discrete values as in the case of a perfect crystal. It is necessary to think in terms of

an average value of the van der Waals' bond. This average value depends on the position of minimum energy occupied by the typical atom in its close-packed arrangement. It is important to realize that the average value of the van der Waals' bond also is proportional to the shear modulus of the material.

For temperatures below T_g the close packed arrangement hardly changes. The average value of the van der Waals' bond does increase with decreasing temperatures; the concomitant increases in shear modulus reflects the increase in bond strength. Since the calculated shear strength is in terms of the shear modulus, the final result does not depend explicitly on temperature as long as the state of close packing remains essentially independent of temperature. The contribution of thermal activation via the Eyring formalism will be considered in another paper.

2.2. The average molecular motion during yielding

The process of yielding begins with the initial application of the stress and ends when a measurable amount of plastic strain is produced. Plastic strain is the irreversible strain observed after unloading the material. In this model of yielding, all the atoms move together in the elastic range so that the nearest neighbours are preserved up to the yield point. On a molecular scale most of the atoms move co-operatively, i.e. in phase with the stress. There is a small amount of out-of-phase motion that is associated with the usual visco-elastic part of the strain. There are some atoms which are more or less strongly bonded than the average, and therefore, lag the applied stress. These out of phase atoms are small in number and are constrained to move in ragged unison with their nearest neighbours.

There may also be localized regions of inhomogeneous strain such as dislocations, disclinations or strophons [2]. It is not thought that the long range motion of these defects is primarily responsible for the yield stress and the attendant plastic strain. It is visualized that the yield point is determined by the stress required to displace practically all the atoms to the state of yielding. However, the plastic strain need not be homogeneous throughout the material. The value of the yield stress does not hinge on the production of a homogeneous plastic strain on a macroscopic scale. What probably happens is as follows: practically all the atoms are brought to the point of yielding

and then small perturbations in strain or bond strength produce localized plastic strain. The plastic strain rate need only be sufficient to satisfy the imposed strain rate of the testing machine.

The co-operative molecular motions during the yield process involves two important conditions:
1. no covalent bonds must be broken, and
2. nearest neighbours are preserved up to the yield point.

The first condition is based on the experimental observation that very few molecular chains are broken at yielding. The second condition is based on the lack of experimental support for the notion that yielding involves nucleation and propagation of discrete defects through the material. Based on these conditions only a few basic types of molecular motion are required in order to conform with a homogeneously applied shear strain. What might appear to be a great complexity of motions, since the amorphous structure seems complex, can be analysed in terms of three types.

2.3. Basic motions of long chain molecules under simple shear

A random array of linear molecules bonded by a van der Waals' force are being considered. The three principal types of motion which occur during the application of a homogeneous simple shear strain without breaking covalent bonds:
1. Shearon — intermolecular shear
2. Roton — intramolecular shear
3. Tubon — motion parallel to the covalent bond.

The resistance of these simultaneous motions to the applied shear stress determines the yield point of the amorphous polymer. First. the geometry of these motions will be discussed. Then the resistance of each of these motions will be calculated. Finally their combined resistance will be determined as it is their combined coordinated motions that determines the yield point.

2.3.1. Shearon motion

Shearon motion occurs where the molecular chain lie in the plane of shear so that parallel planes of atoms shear passed each other. The covalent bonds offer no restraints to this motion. Each atom in the plane passes from its initial site of minimum energy to an adjacent energy well. The displacement of all atoms in a plane is the same except for a small amount of out-of-phase motion. The path
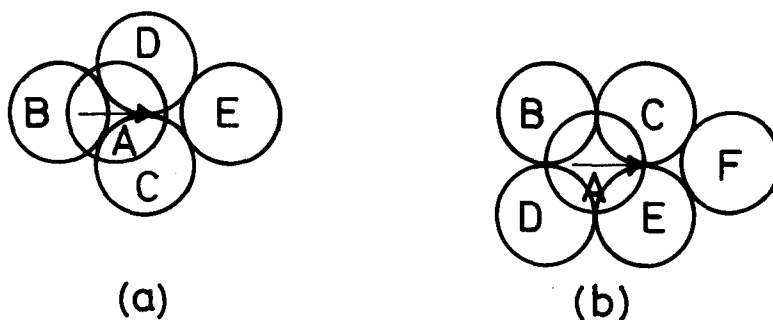
Figure 1 (a) Typical localized close packing. Atom A shears relative to plane BCDE. (b) An approximately close packing. Atom A shears relative to plane BCDEF.

of a typical atom is shown in Fig. 1a which represents the typical close-packed arrangement throughout the polymer.

In Fig. 1a atoms B, C, D and E form the shear plane. Atom A initially lies in the minimum energy site formed by atoms B, C and D and is directed, by the applied shear stress, through the valley between atoms C and D. The major resistance is the attractive force between atoms A and B. The yield stress corresponds to the point where the attractive force between atoms A and B is a maximum. Then atom A ends up in the adjacent energy well formed by atom C, D and E, thus producing plastic strain.

The close packed arrangement shown in Fig. 1a will not be the same throughout the polymer. Fig. 1b shows a slight modification where the initial site of the A atom is formed by a less close packed nest of four atoms B, C, D and E. Under the shear stress, the resistance to the motion of atom A comes from the attractive forces from atoms D and B as A passes through the valley between atoms C and E and finally falls into the adjacent energy well formed by atoms C, E and F. The difference in shearon resistance in Fig. 1a is not greatly different than in Fig. 1b.

2.3.2. Roton* motion

Roton motion involves the co-operative shear between atoms joined by the covalent bond. Roton shear occurs for molecular chains that intersect the plane of shear and are initially inclined against the direction of the shear stress. In Figs. 2a and b is a molecule with the covalent bond along a–b and a–b is inclined against the arrows representing the direction of shear. As the shear stress is applied the chain of atoms rotate as illustrated in Figs. 2a to c.

The roton motion is such that the length of the covalent bond remains essentially constant. It is to be noted that the atoms adjacent to the roton may move as shearons or rotons and they maintain the close-packed structure. Note that during roton motion the covalently bonded atoms shear co-operatively by rotating about a point centred on the covalent bond.

The basic resistance to roton motion is about the same as for a shearon. If in Fig. 1a atom A were covalently bonded to atom C, roton motion would occur such that atoms A and C shear in opposite directions. The basic resistance to the roton motion is still the attractive force between atoms A and B. The difference between shearon and roton motion can be seen in Fig. 1a. In shearon motion atom A moves while the adjacent plane BCDE need not move, but in roton motion it must move as A moves.

For a flexible chain, the entire length of chain does not have to move for roton motion to occur. As shown by the roton in Fig. 3, only the portion of the chain bc underwent roton motion. The entire chain may have rotated nearly up to the yield strain which is only about 17%, but the final yielded state would occur in that part of the material which was weakest. A point of weakness may also be viewed as a place where the stress is concentrated. The calculation of the yield stress does not require that the plastic strain be homogeneous, but only that all the atoms be brought up to the point of yielding under an almost homogeneous elastic strain.

When part of a molecular chain is inclined in the direction of the shear stress as in the portion bc in Figs. 3 and 2c, it is in a sessile state. In the sessile state the roton cannot rotate further with-

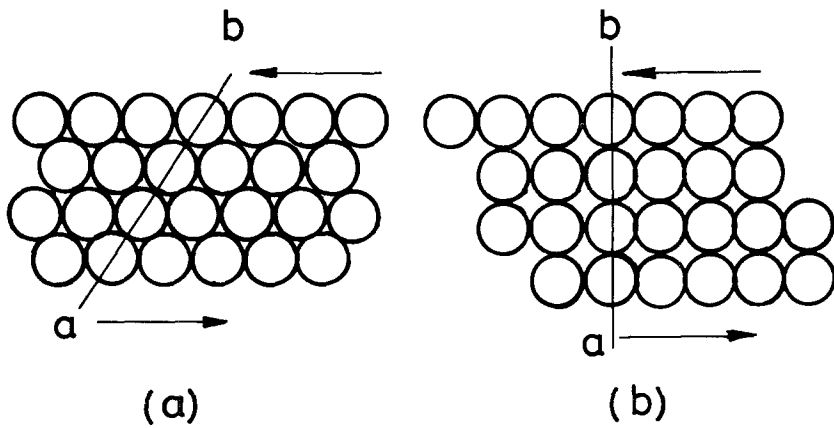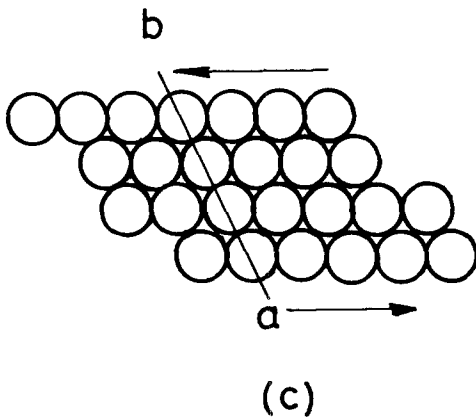*As pointed out by Professor F. C. Frank roton had been used for a quantum of rotational energy.

(a)

(b)

Figure 2 Roton motion going from (a) to (c).

(c)

out stretching the strong covalent bonds. Thus, we can classify a roton as being glissile if it is inclined against the shear stress and sessile if it is inclined in the direction of the shear stress. Shearon motion in the vicinity of a sessile roton becomes inhibited so that a localized inhomogeneous strain occurs.

The molecular chain may be part shearon and part roton as shown in Fig. 4a. The part ab is a glissile roton and the part bc is a shearon. The part bc does not have to be in the shear direction to be a shearon; it need only lie in the shear plane.

There are various possibilities for the motion of the combined shearon and roton in Fig. 4a. All of length ab may undergo roton motion until it becomes sessile as in Fig. 4b. Now shearon bc cannot move without pulling the length of chain ab along with it. The force required to pull on the chain ab adds to the shear resistance of the shearon. As will be described below the pulling of a chain relative to stationary neighbouring atoms is called a tubon.

Another possible motion for the shearon—roton combination in Fig. 4a is shown in Fig. 4c where the motion of the shearon creates a bend in the portion ab at the point d so that, in effect roton motion occurred along db. This roton motion could travel toward point a until ab became completely sessile.
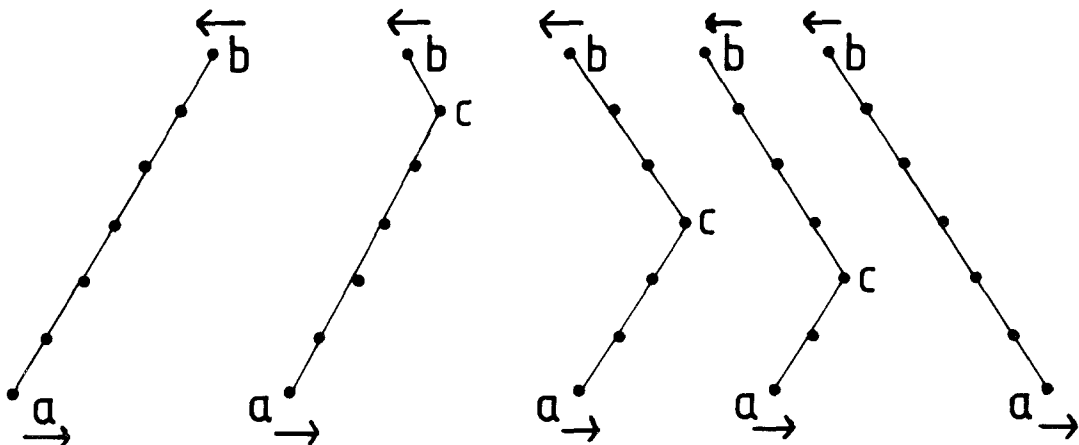

Figure 3 Roton motion occuring gradually along the chain ab going from left to right along the figure. bc is the part of the chain that has undergone roton motion.
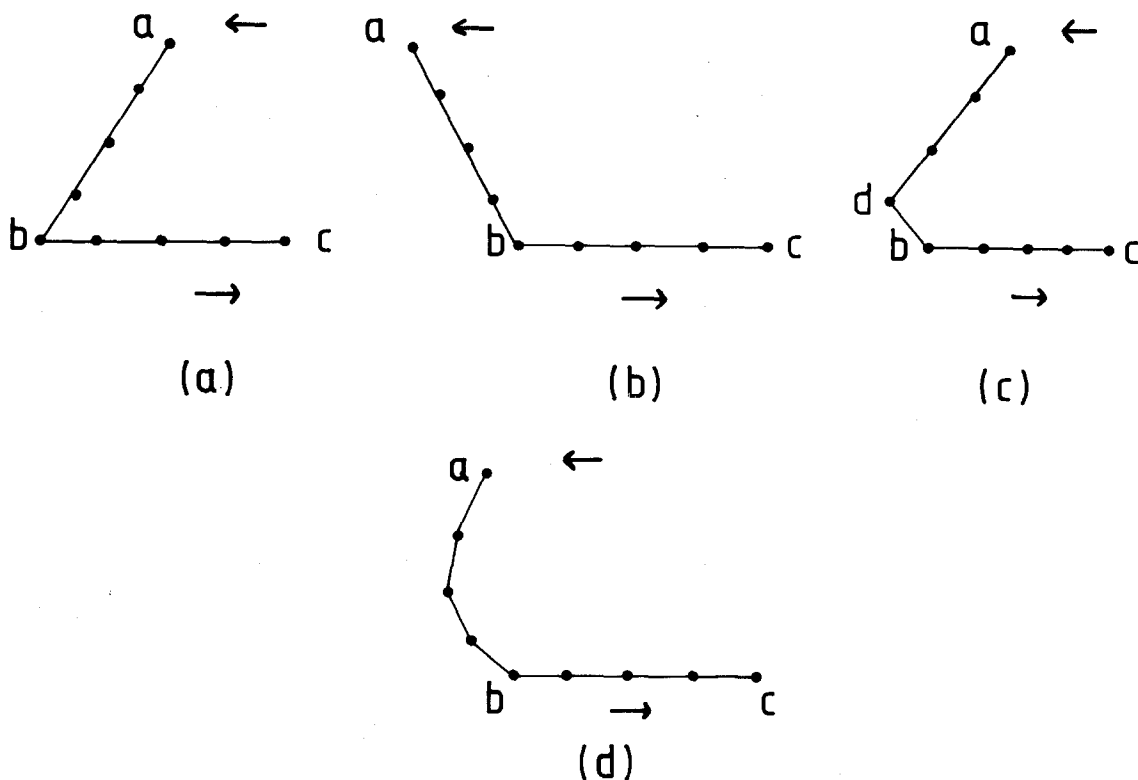
Figure 4 Combined roton and shearon motions. (a) is the initial conformation, (b) roton motion with or without shearon motion of bc, (c) shearon motion of bc with roton motion along bd, (d) shearon motion along bc with point a fixed so that chain dragging occurs along ab.

There is another possibility of motion for the shearon—roton combination shown in Fig. 4d. The shearon bc displaces and the chain ab is curved and dragged so that a complex inhomogeneous array of atomic displacements occur around the dragged chain. This mode is not expected as it requires too much energy.

2.3.3. Tubon motion

Fig. 5 shows a molecular chain whose parts ab and cd lie in different shear planes and they are connected by a sessile roton bc. Under the applied shear stress, ab and cd translate to the left and right, respectively, while the chain is pulled upward at b and pushed upward at c. This co-ordinated motion causes the chain bc to move through a tube of stationary neighbours. Therefore, this motion is called a tubon. The tubon motion is non-affine and does not contribute to the macroscopic shear strain. Also the tubon motion does not interact with the applied shear stress. As a result the tubon produces an added resistance to that of the connecting shearons.

The tubon moves relative to its stationary nearest neighbours. For the case of closest packing each atom that moves as a tubon experiences a change of about 7 nearest neighbours compared to 1 for a shearon. The total resistance of the tubon is proportional to its length. The tubon resistance must be added on to that of the shearon in order to determine the overall resistance of the shearon.

Tubon motion produces another type of non-affine deformation. Tubon motion in conjunction with the shearon motions, as in Fig. 5, shows shearons ab increasing in length and cd simultaneously decreasing. This causes a net flux of atoms from ab and toward dc in the form of a non-affine diffusive type of motion. Altogether tubon motion produces a circulation of atoms in the form of a concentrated movement along the tubon and the diffusive motion between the shearons. It is the accompanying shearon motion that contributes to the macroscopic shear strain.

Another feature of tubon motion should be observed. When an atom enters or leaves a tubon from or to the adjoining shearon, it turns the corner. This turning motion will be a combination of roton and tubon motion depending on the
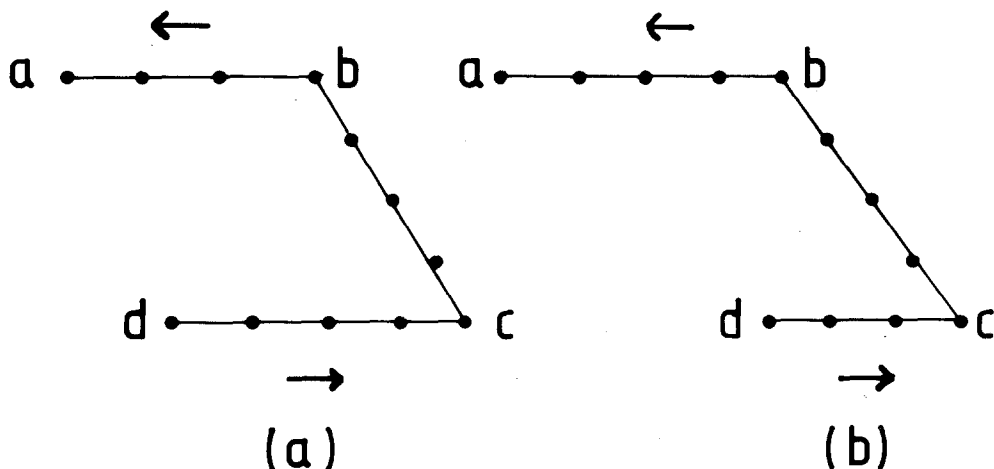
Figure 5 Shearon plus tubon motion (a) is the initial conformation.

curvature of the corner which in turn depends on the flexibility of the molecular chain.

Fig. 6 shows examples of glissile and sessile tubons. In Figs. 6a and b are glissile tubons with the motion from c to b in Fig. 6a and from b to c in Fig. 6b under the co-ordinated motion of the shearons. Figs. 6c and d show sessile tubons since the chain bc is being pulled from opposite directions in Fig. 6c and compressed from opposite directions in Fig. 6d.

Shearon, roton, and tubon motion may occur along the length of the same molecule. Fig. 7a shows the initial conformation. In Fig. 7b roton and shearon motion has occurred. Fig. 7c shows the subsequent conformation after tubon and shearon motion. No doubt there are many other combinations of motion, but the focus on shearons, rotons, and tubons as the unit processes helps us to visualize the individual molecular motions that produce the observed macroscopic strain.
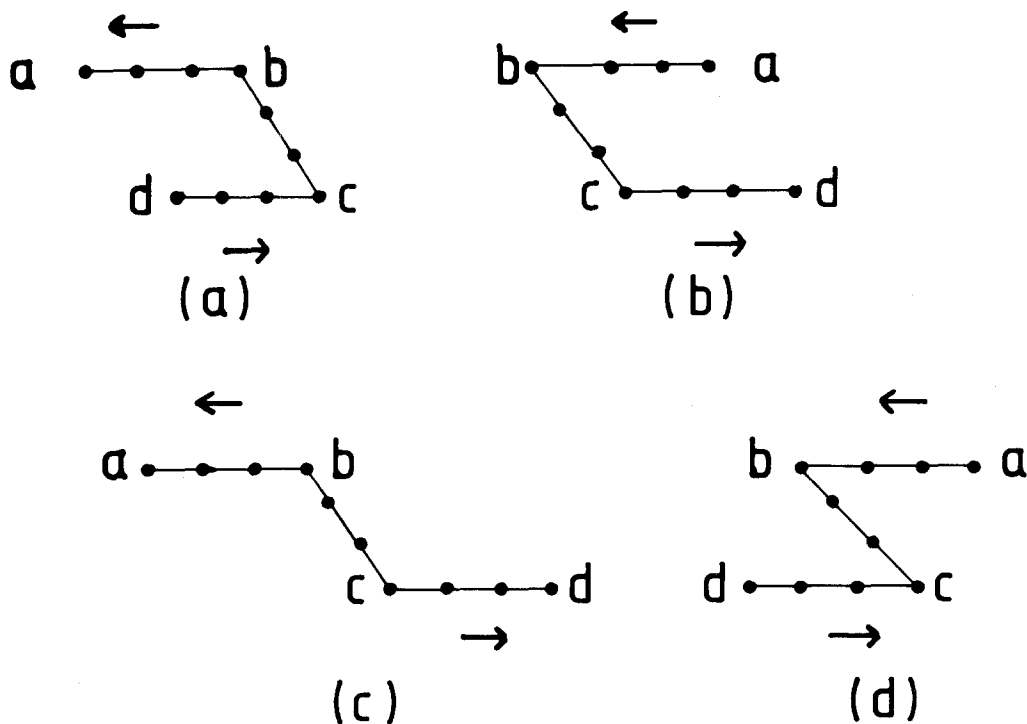

Figure 6 (a) and (b) glissile tubon motion with shearons (c) and (d) sessile conformations.
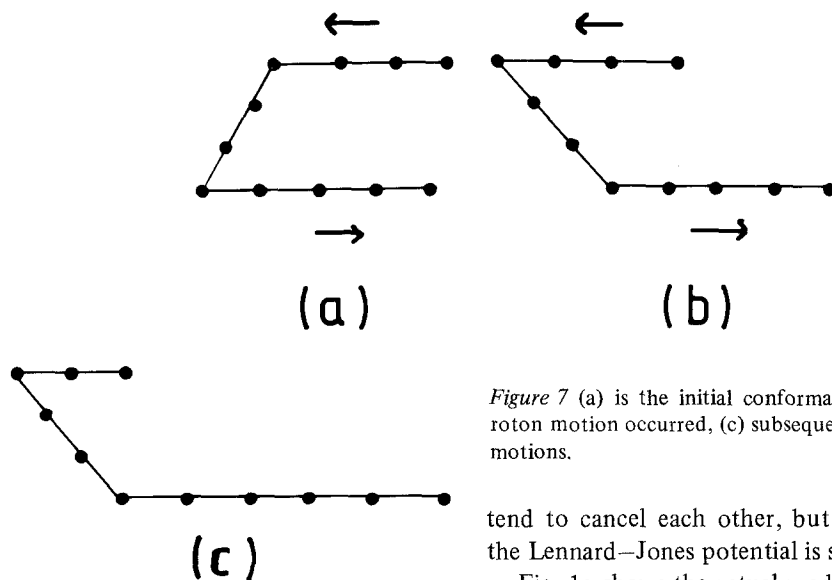
(a)

(b)

(c)

Figure 7 (a) is the initial conformation, (b) shearon and roton motion occurred, (c) subsequent shearon and tubon motions.

Another important observation about these three motions is that they tend to produce molecular orientation. During roton motion the chain rotates toward the same direction relative to the applied stress. If during tubon motion, a connecting shearon increases in length as the tubon length decreases, this combined motion produces an overall increase in molecular orientation. Pure shearon motion alone neither increases or decreases the degree of orientation in simple shear.

2.4. Stress to move a shearon

Fig. 8 is a two-dimensional view of a shearon. The plane of atoms EAF move co-operatively relative to the shear plane of atoms GBCD. Taking atom A as the typical atom, it is seen that when A moves out of the energy well formed by B and C its motion is resisted by the stretching of the AB bond. The AC bond is compressed. The AG and AD bonds may be neglected partly because they
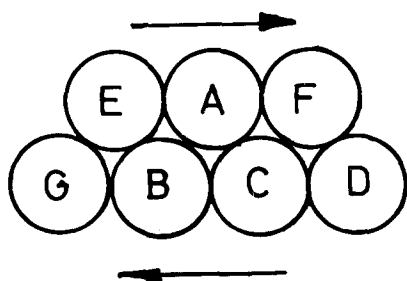
tend to cancel each other, but primarily because the Lennard–Jones potential is short range.

Fig. 1a shows the actual model used for the calculation. The model is based on the local close packing being the same as in a face centred cubic structure for $\{1\,1\,1\}\,\langle 1\,1\,2\rangle$ shear. As the A atom moves under the applied shear, the AC and AD bonds become repulsive and the AB bond is attractive. The much longer AE bond can be neglected since the maximum resistance to shear occurs at a shear strain of 17% without thermal activation and at about 7% strain in the actual material. Tyson did a computer calculation for a face centred cubic crystal with a Lennard–Jones potential using about 51 atoms and his results are only about 20% less than the three bond model of Fig. 1a. It is interesting to present the calculation for the three bond model because it gives a direct insight into the resistance of the shearon. The assumption that the local structure of the shearon is the same as that in a face centre close packed crystal means that the calculated results are an upper bond because the random close packing of the glassy polymer would be expected to offer less resistance to shearon motion than that in a perfect crystal.

Fig. 9 shows the coordinate system for the calculation. Points A, B, C and D represent the centre of the atoms shown in Fig. 1a under zero stress. The shear stress is applied parallel to the BCD plane in the y direction. The A atom displaces along AA' and the atoms B, C and D are assumed to remain fixed. The coordinates of the atoms are given in Table I. Let $a_1 =$ the length of the AB bond, $a_2 =$ the length of the AC and AD bonds, $S_1 =$ the force of the AB bond, $S_2 =$ the force of the AC and AD bonds, $\gamma = (3/2)^{1/2} d/a_0 =$ shear strain, and $F =$ shear force on atom A in y direc-

Figure 8 Illustrates shearon motion with co-operative shear of atoms E, A and F relative to atoms G, B, C and D.
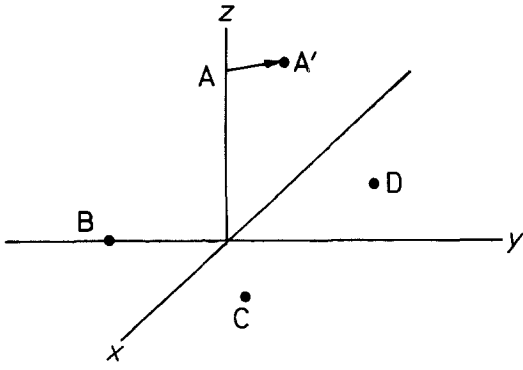
Figure 9 Coordinate system for Table I.

tion. The length and direction of the bonds can be calculated from the coordinates in Table I.

A summation of forces on atom A in the z direction gives

$$S_1/a_1 + 2S_2/a_2 = 0 \qquad (2)$$

when no force is acting perpendicular to the shear plane. The summation of forces on A in the y direction gives

$$\frac{S_1}{a_1}\left(\frac{-a_0}{(3)^{1/2}} - d\right) + \frac{2S_2}{a_2}\left(\frac{a_0}{2(3)^{1/2}} - d\right) + F = 0 \quad (3)$$

a_1 and a_2 determine γ where

$$\left(\frac{a_1}{a_0}\right)^2 - \left(\frac{a_2}{a_0}\right)^2 = (2)^{1/2}\gamma \qquad (4)$$

Combining Equations 2 and 3 give

$$F = \frac{(3)^{1/2}}{2} S_1 \left(\frac{a_0}{a_1}\right) \qquad (5)$$

The energy of a van der Waals' bond may be represented by the Lennard–Jones potential

$$E = B\left[-2\left(\frac{a_0}{a}\right)^6 + \left(\frac{a_0}{a}\right)^{12}\right] \qquad (6)$$

where B is the energy when $a = a_0$. The force of the bond is given by

$$S = \frac{dE}{da} = \frac{12B}{a_0}\left[\left(\frac{a_0}{a}\right)^7 - \left(\frac{a_0}{a}\right)^{13}\right]. \quad (7)$$

TABLE I Coordinates of the atoms. a_0 is the equilibrium bond length, d is the shear displacement, and h is the increase in distance of atom A above the shear plane

Atom	x	y	z
A	0	d	$h + (2/3)^{1/2}a_0$
B	0	$-a_0/(3)^{1/2}$	0
C	$a_0/2$	$a_0/2(3)^{1/2}$	0
D	$-a_0/2$	$a_0/2(3)^{1/2}$	0

Substituting Equations 7 into 5.

$$F = \frac{6(3)^{1/2}B}{a_0}\left[\left(\frac{a_0}{a_1}\right)^8 - \left(\frac{a_0}{a_1}\right)^{14}\right]. \qquad (8)$$

The yield point corresponds to the maximum value of F. Setting $dF/da_1 = 0$, the value of (a_0/a_1) at the yield point is

$$\left(\frac{a_0}{a_1}\right)_y = \left(\frac{4}{7}\right)^{1/6} \qquad (9)$$

and

$$F_{max} = \frac{6(3)^{1/2}B}{a_0}(0.203) \qquad (10)$$

From Equations 2, 4 and 9

$$\left(\frac{a_0}{a_2}\right)_y = 1.0146 \qquad (11)$$

and the yield strain is

$$\gamma_y = 0.165 \qquad (12)$$

It is useful to obtain the shear stress for yielding Υ_{max} in terms of the shear modulus.

The shear stress, $\Upsilon = F/A$, where A is the area of shear plane per atom. The shear modulus is defined as

$$G = \left(\frac{d\Upsilon}{d\gamma}\right)_{\gamma=0} \qquad (13)$$

By differentiating Equation 8 with respect to γ and making use of Equations 2, 4 and 13

$$\frac{B}{a_0 A} = \frac{G}{12(6)^{1/2}} \qquad (14)$$

and from equation 10

$$\Upsilon_{max} = 0.0718G \qquad (15)$$

G is proportional to $(3/2)^{1/2}B/a_0A$ which is the bond energy per unit volume to the cohesive energy density of the material.

The computer calculation by Tyson using 51 atoms gave $\Upsilon_{max}/G = 0.061$ and $\gamma_y = 0.13$ for a perfect face centred cubic crystal. If the AE bond (Fig. 1) were included in the calculation the result in Equation 15 would be reduced to that of Tyson's solution because the AE bond assists the applied stress. We will use Tyson's results as an upper bound for the shear resistance of a shearon.

2.5. Calculation of the relative amounts of each motion

It is assumed that the yield stress is determined by the resistance of the co-operative homogeneous

motion of all the atoms in the material. The co-operative motion is assumed to take place by the combined shearon, roton and tubon motion as described in Section 2.3. The calculation is based on an estimate of the fractions of the total motion that is contributed by shearons, rotons and tubons. Then if the shear resistance is known for each of the three motions, the overall shear resistance of the polymer can be calculated.

The random close packed structure can be visualized as a random fine grain polycrystalline face centred cubic crystal. There are six $\langle 1\,1\,0 \rangle$ close packed directions. The direction of the covalent bond in the back bone is always a close packed direction. The number of nearest neighbours in a face centred cubic crystal is 12. For a random close packed structure of spherical atoms it is about 11. For a random close packed array of linear chains consisting of spherical atoms, it is estimated to be about 10 because the restraints of the covalent bond give a less close packing than in a random structure of spherical atoms. The difference in density betweeen the amorphous and crystalline state is consistent with this estimate. For example the density of a perfect crystal of polyethylene (PE) is 1.00 and the density of liquid PE extrapolated to room temperature is $0.86\,\mathrm{g\,cm}^{-3}$.

If on average there are 10 nearest neighbours, then the two nearest neighbours are covalently bonded. Therefore, 1/5 of the six $\langle 1\,1\,0 \rangle$ directions are along the covalent bond.

The slip planes are $\{1\,1\,1\}$. Three $\langle 1\,1\,0 \rangle$ directions lie in a slip plane and three are out of it. Therefore, $1/5 \times 3/6$ or $1/10$ equal the fraction of nearest neighbour bonding directions that are out of the slip plane and are in a convalent bond directions. This is the fraction of the total motion that involves rotons and tubons. Since there are as many tubons as rotons, this estimate gives the following results: 9/10 shearons, 1/20 rotons, and 1/20 tubons.

Another estimate can also be made. Consider the unit shearon process illustrated in Fig. 1a. If the bond between atom A and B is a van der Waals' bond, shearon motion can occur; otherwise a roton or tubon exists. If the number of nearest neighbours is 10 then two are covalent bonds thus 2/10 of the motions are roton and tubon and of these half should be tubons. Consequently there would be 8/10 shearon 1/10 roton and 1/10 tubon motion.

Both estimates indicate that shearon motion predominates. The predominance of shearon motion can be observed by the following experiment. Place long strings of beads randomly in a flexible transparent bag. Shear the bag and it will be observed that the dominant motion consists of shearons and rotons. The amount of chain pulling which is characteristic of tubon motion is relatively small. However, the resistance of tubon motion is much greater than that for shearons and rotons.

2.6. Calculation of the yield point

Since all the atoms are assumed to move co-operatively, the yield point is the sum of the resistances from each type of motion.

$$\frac{\Upsilon_{\max}}{G} = f_{\mathrm{S}}\frac{\Upsilon_{\max}(S)}{G} + f_{\mathrm{R}}\frac{\Upsilon_{\max}(R)}{G} + f_{\mathrm{T}}\frac{\Upsilon_{\max}(T)}{G}$$
(16)

where f_{S}, f_{R} and f_{T} are the fractions of each type of motion as estimated in the previous section. $\Upsilon_{\max}(S)$ etc., are the shear resistances associated with each type of motion. $\Upsilon_{\max}(S)/G$ was calculated above using three nearest neighbour model. It would be better to use Tyson's [12] result for the ideal strength of a f c c crystal as this would be an upper bound for shearon motion in a random close packed structure where $\Upsilon_{\max}(S)/G = 0.061$.

The resistance of roton motion is about the same as for shearon motion. If in Fig. 1a, atom A is covalently bonded to atom C or D then roton motion is involved. The primary resistance to the motion of atom A arises from the stretching of the AB bond. This stretching force is not much different for roton or shearon motion because the bond lengths between A and C and A and D remain little changed whether they be covalent bonds or van der Waals' bonds in compression.

The tubon motion is much greater than that for a shearon. During shearon motion the typical atom breaks one nearest neighbour bond, but in tubon motion an atom breaks seven nearest neighbour bonds. This result can be obtained by observing that two nearest neighbour atoms in an f c c crystal have five nearest neighbours in common, excluding themselves. Thus tubon resistance would be at least seven times stronger than for a shearon on this basis. There is also an additional resistance to tubon motion besides that required to break bonds. During tubon motion all of the surrounding

atoms must be expanded in order to allow an atom to pass to an adjacent site in the direction of the covalent bond. This resistance would approximately correspond to the energy required to expand a cylindrical hole in an infinite solid. The expansion would depend on the opening required by an atom as it passed through its saddle point. The resistance for breaking seven bonds should be approximately seven times for a shearon or $7 \times [\Upsilon_{max}(S)/G] = 0.43$. Adding the resistance of expanding the surrounding atoms $[\Upsilon_{max}(T)/G]$ would be greater than 0.43. The question arises as to whether tubon motion can occur with a lower resistance than this value.

The are two existing calculations for the stress to pull a molecular chain through a polymer. Kausch and Becht [14] calculated the force to pull an infinitely long molecule from a crystal of polyethylene. They calculated a force of 1.37×10^{-4} dynes.* The Kausch and Becht calculation was for an infinite chain and involved a co-operative motion along the chain analogous to a dislocation type motion. They state that the resistance for the infinite molecule is 15.8 times that of a mer. Tubons have a finite length and the resistance of the tubon depend on its length where the length is determined by the separation of the connecting shearons. Since the fraction of tubons and rotons are only about 1/5 to 1/10, then it is not expected that the length of a tubon will be more than 10 mers long. Therefore, the resistance of a mer of a tubon is estimated to be $1.37 \times 10^{-4}/$ 15.8 dynes. Now the resistance of the tubon adds onto the shear resistance of the adjoining shearon. Therefore,

$$\frac{\Upsilon_{max}(T)}{G} = \frac{1.37 \times 10^{-4}}{15.8 \times area\ (S) \times G} \qquad (17)$$

area (S), the area of a shearon, is the diameter of the chain times the repeat distance along the chain $= 5.4 \times 10^{-16}\ cm^2$. G, shear modulus of polyethylene, is $4.3 \times 10^9\ N\ m^{-2}$ at 0 K

$$\frac{\Upsilon_{max}(T)}{G} = 0.37. \qquad (18)$$

This value is about equal to the last result based on the breaking of seven bonds.

Argon [3] calculated the stress to pull a chain within an amorphous polymer. His yield point calculation is based only on a tubon type motion.

*1 dyne = 10^{-5} N.

He assumed that the motion occurred via the mechanism of. nucleating and propagating a pair of wedge disclination. His result in a later paper is [10]

$$\frac{\Upsilon_{max}}{G} = \frac{0.077}{(1 - \nu)} \qquad at\ 0\ K \qquad (19)$$

where ν = Poisson's ratio. A best value for $\nu = 0.37$ rather than 0.3 as used by Argon so that

$$\frac{\Upsilon_{max}}{G} = 0.122 \qquad (20)$$

We now can calculate the yield point using Equation 16. A lower limit comes from Argon's result and the estimate of 5% tubon motion, and the upper limit uses Kausch and Becht's results with 10% tubon moton

$$\frac{\Upsilon_{max}}{G} < 0.064 - 0.092 \qquad (21)$$

The lower limit for Υ_{max}/G should be less than 0.064 since the value of $\Upsilon_{max}(S)/G$ that was used is an upper limit since it is based on the perfect crystal. It is expected that the tubon resistance depends on packing more than the shearon resistance. Since tubon resistance involves an expansion of material around the tubon, it would depend on both G and Poisson's ratio. The theoretical results will now be compared to existing experimental data.

3. Comparison of theory and experimental data

A review was made of the data on yield point against temperature for linear polymers. Most data was for yielding under a uniaxial stress. The yield process was generally interrupted by brittle fracture at temperatures. The yield points were extrapolated to 0 K using a linear extrapolation of the data points at the lowest temperatures. The yield point in simple tension or compression was converted to a shear yield point. The conversion required an assumption about the yield criterion for the polymer. The work by Bowden and Jukes [15] was used as a guide as to whether a modified von-Mises or modified Tresca criterion was applicable.

$$\Upsilon_{max} = \frac{[1 \pm \mu/(3)^{1/2}]\sigma_{max}}{(3)^{1/2}}$$

modified von-Mises

TABLE II Yield points at 0 K by extrapolation

Polymer	Source	Test	σ_{max}(GPa)	Yield criterion	μ	Υ_{max}(GPa)
PS	[16]	compression	0.30	Tresca	0.25	0.13
PS	[17]	compression	0.27	Tresca	0.25	0.11
PMMA	[18]	compression	0.82	von-Mises	0.158	0.43
PMMA	[19]	compression	0.87	von-Mises	0.158	0.45
PMMA	[20]	compression	0.73	von-Mises	0.158	0.38
PC	[21]	shear	0.18	–	–	0.18
PC	[22]	tension	0.26	von-Mises	0.12	0.16
PC	[23]	tension and compression	0.30 (av)	von-Mises	–	0.17
PET	[22]	tension	0.24	von-Mises	0.09	0.15
PCTFE	[24]	tension	0.25	von-Mises	0.12	0.15
PE (high density)	[25]	tension	0.20	von-Mises	below 0.05	0.12
PP (isotactic quenched)	[26]	tension	0.11	von-Mises	0.12	0.068

$$\Upsilon_{max} = \frac{(1 \pm 2\mu/3)\sigma_{max}}{2}$$

modified Tresca

where $\mu = d\Upsilon_{max}/dp$ the change in shear yield point with hydrostatic pressure and σ_{max} is the yield point under a uniaxial stress. The positive sign is for tension and the negative for compression.

The results are shown in Table II. The von-Mises criterion was used when it was not known which one applied because most investigations favour the von-Mises criterion. The μ values from the Bowden and Jukes [15] paper were used. If μ was not available, then an average value of 0.12 was used.

The shear modulus at 0 K was obtained from the literature (Table III). The shear modulus was used which most closely corresponded to the morphology of the polymers presented in Table II.

TABLE III Shear modulus at 0 K and Poisson's ratio

Polymer	Source	G(GPa)	Source	ν
PS	[27]	1.7	[42]	0.33
PS	[28]	1.8	[41]	0.33–0.036
PS	[29]	1.7		
PMMA	[30]*	3.3	[31]	0.34
PMMA	[31]	3.0		
PC	[32]*	3.3	[33]	0.43
PC	[33]	3.5		
PET	[34]*	1.5		
PET	[22]	1.7		
PCTFE	[35]*	2.3		
PE (high density)	[36]	4.0		
PE	[37]*	4.7		
PP (isotactic-quenched)	[38]*	2.3		

*Data obtained from N. G. McCrum et al. [40].

The extrapolation of the data to 0 K was done with greater confidence than for the yield point because the data generally existed for temperatures down to about 77 K. Where data existed from several investigations, those results were omitted which greatly varied from the average value.

Poisson's ratios for the polymers are also shown in Table III. The values are for room temperature. As shown by Yee and Takemori [31], Poisson's ratio does not vary greatly with temperature. The average value of Poisson's ratio from all the available data was 0.38 ± 0.04.

The values of Υ_{max}/G at 0 K are shown in Table VI as calculated from Tables II and III. The average values of Υ_{max} and G were used for each polymer. Also shown in Table IV are the predictions by Argon [10] based on the equation $\Upsilon_{max}/G = 0.077/(1 - \nu)$. Argon used 0.3 for Poisson's ratio but in Table IV the actual values are used or if not available an average value of 0.37. Argon also systematically reduced the experimental data by 8 to 20% in order to get a better fit with his theory. Table IV shows that the present theory is in better agreement with the experimental data than the Argon theory. The Argon theory gives a high value because it is based only on tubon type motion. It is important to realize that there are significant differences among the polymers which no doubt are related to the detailed chemistry of the molecular chain and which has not been considered in the theory.

4. Discussion
The displacment of the molecules in an amorphous polymer under a shear stress in the elastic regime

TABLE IV

Polymer	Υ_{max}/G (Experimental)	$\Upsilon_{max}/G = \dfrac{0.077}{1 - \nu}$ (Argon [10])
PS	0.069	0.12
PMMA	0.133	0.11
PC	0.050	0.14
PET	0.094	0.12
PET*	0.088	0.12
PCTFE	0.065	0.12
PE (high density)	0.027	–
PP (isotactic-quenched)	0.030	0.12
Average (excluding PE)†	0.076 ± 0.03	Present theory < 0.064–0.092

*[3] based on yield data by Foot and Ward.
†PE was excluded because it is highly crystalline.

has been analysed in terms of three modes of motion, shearons, rotons, and tubons. The shearon or intermolecular shear accounts for about 90% of the motion and the remaining 10% is divided between rotons and tubons. All three modes occur co-operatively so that the strain up to the yield point is essentially homogeneous except for a small amount of motion which is out of phase with the stress. This out of phase motion produces the internal friction effects. The important point about the strain up to the yield point is that it is not considered to be produced by the nucleation and long range propagation of a defect. The point is supported by the fact that the experimental values of Υ_{max}/G agree with theoretical value based on homogeneous strain up to the yield point. The existence of non-homogeneous plastic strain in the form of shear bands does not invalidate the existence of nearly homogeneous elastic strain shear up to the yield point.

The theoretical results for Υ_{max}/G applies at all temperatures below T_g in that it represents the value of Υ_{max}/G that is expected in the absence of thermal activation. It is the limiting value expected at very high strain rates. The theory may, however, not be applicable near T_g because diffusive non-homogeneous modes of deformation may predominate at higher temperatures.

It is important to note that temperature effects the yield point in two ways:

1. There is the intrinsic effect from the change in modulus with temperature and this is accounted for in the theory by using the ratio Υ_{max}/G as the measure for yielding.

2. There is the extrinsic effect of thermal activation as described by the Eyring formalism. In another paper the effect of thermal activation will be considered. The present model provides a molecular interpretation for the activation energy to be used in the Eyring equation.

The Yannas and Lunn [2] model of chain twisting (strophons) is also based on the Lennard–Jones potential and predicts a value of 0.03 for Υ_{max}/G. In this model tubon motion is neglected. Also it is not clear how the twisting of individual chains is related to the macroscopically applied shear stress.

The Bowden and Raha [4] theory is not a molecular model in that it considers the polymer as a continuum. The dislocation is introduced as the mechanism of strain. We do not think that dislocation motion theory offers the best approach for understanding yielding in amorphous polymers. A direct approach in terms of the totality of molecular motions appears to be more appropriate. The Argon model is based essentially on tubon type motion and completely neglects the dominant low resistance intermolecular shear provided by shearons. That is one reason why the Argon theory over estimates the experimental values of Υ_{max}/G. The other reason is that Argon used linear elastic theory. Argon's theory offers a means for estimating tubon resistance.

The present theory has one outstanding deficiency in that chain flexibility is not part of the theory. No doubt roton resistance and the resistance of a chain link as it turns the corner from tubon to shearon motion would depend on chain flexibility. Perhaps the range of experimental value for Υ_{max}/G for the various polymers depends partly on differences in chain flexibility. In this model, roton motion was presented in terms of a rigid rod rotating with the applied shear. Most likely the roton moves in a more flexible way.

Another weakness of the theory is in the crude-

ness of the calculation for the relative amounts of shearon, roton and tubon motion. That shearon motion dominates is partly based on analysis and partly on the intuitive visualization of the motion of a random array of flexible chains under an applied shear stress. The division of motions into shearons, rotons, and tubons is a useful device for analysing the complexities of motions during the shearing of an amorphous polymer.

Acknowledgements

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