

# Attempt to correlate the formation of free volume and the plastic deformation process in glassy polymers

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Both the formation of free volume and the elementary motion characterizing the plastic deformation in the glassy state are described here by the same molecular process, consisting of the transition of a given number of chain segments from fundamental to activated states. Using this basic assumption, a model is proposed which makes use of classical laws of thermodynamics. Five parameters need to be adjusted to take into account the thermodynamic properties related to the free volume: one more is necessary to characterize the molecular process of plastic deformation. The pressure dependence of  $T_g$  and the difference between the specific volumes found in the glassy state from isothermal and isobaric measurements can be calculated from the model. Fairly good agreement is found between the theoretical and experimental values of these quantities. The physical meaning of constants belonging to a previously-proposed yield criterion is clarified, and these constants are given as a function of the molecular process. Moreover, the treatment confirms that the glass transition temperature is related to a constant fraction of activated segments and not to a constant value of the free volume.

## INTRODUCTION

Since the early work of Williams, Landel and Ferry<sup>1</sup>, many treatments of the glass transition have been proposed. Some are complex, none is convincing. Here, we present a new analysis of the concept of free volume; the glass transition is formulated, supported by classical equations and simple assumptions. An attempt is made to show that plastic deformation in the glassy state and the formation of free volume are governed by the same process.

Numerous papers, both theoretical<sup>2-4</sup> and experimental<sup>5-7</sup>, admit that above the glass transition temperature  $T_g$ , the molecular motions occurring in a polymer are related to free volume. From dilatometry performed under hydrostatic pressure<sup>7-9</sup>, it has been shown that Ehrenfest's law is not valid for polymers. A theory implying a single ordering parameter cannot hold. Ehrenfest's law implies that:

$$\frac{dT_g}{dp} = \frac{\Delta\beta}{\Delta\alpha} \quad (1)$$

where  $p$ ,  $\Delta\beta$  and  $\Delta\alpha$  denote respectively pressure and increase of compressibility and thermal expansivity above  $T_g$ . Several investigators<sup>10-12</sup> have shown that the theory of activated processes<sup>13</sup> is capable of giving a correct description of motion in glassy polymers, but a correlation between this theory and free volume has not yet been attempted.

We propose a model which takes into account both thermodynamic theory and plastic deformation in the glassy state; this model leads to relations previously given empirically by Simha and Boyer<sup>14</sup> and shows how  $T_g$  varies with hydrostatic pressure. The pressure dependence of the specific

volume,  $V$ , is analysed and  $\Delta v$ , the observed difference in specific volume between values obtained from isothermal and isobaric measurements, is explained allowing  $\Delta v/V$  to be calculated. Numerical results agree well with data in the literature.

Finally, we give an interpretation of the nature of the elementary process of plastic deformation in the glassy state, suggested by the model. The calculated values for the parameters characterizing the plastic deformation are observed to fit the data.

## MODEL

The assumption is made that a chain segment may lie either in a fundamental state not related to any free volume, or in  $m$  activated states associated with the formation of free volume. For example, these activated states may correspond to flexed bonds.

Let  $Q$  be the mean increase in energy and  $v_0$  the mean free volume which an activated segment needs and let us assume a one-to-one correspondence between  $v_0$  and such segments. Above  $T_g$ , when complete temperature equilibrium is reached, the fraction of activated segments,  $P$ , may be expressed to a first approximation by:

$$P = \frac{m \exp(-Q/RT)}{1 + m \exp(-Q/RT)} \quad (2)$$

where  $T$  denotes the absolute temperature and  $R$  the gas constant. Equation (2) may be used to compute  $P$  as a function of  $RT/Q$  for several values of  $m$ . Results are shown graphi-

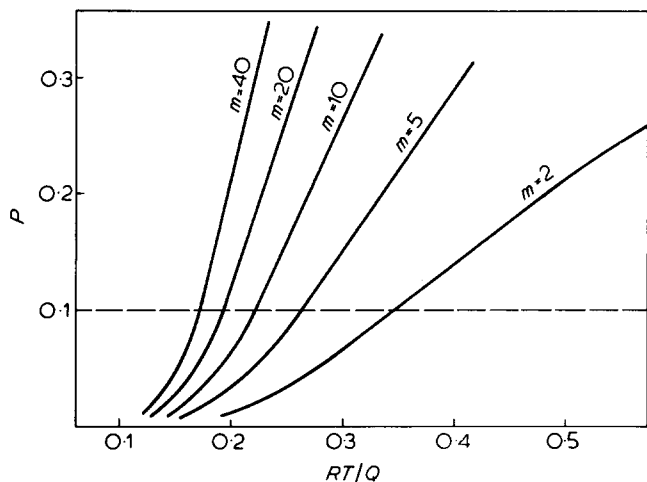


Figure 1  $P$  as a function of  $RT/Q$  for several values of  $m$  (calculated from equation 2)

cally in Figure 1 where it can be seen that the different curves reduce to straight lines for  $P \geq 0.1$ .

$P$  gives rise to a dilatation defined as follows:

$$\frac{\Delta v}{V} = \frac{v_0}{V_0} P \tag{3}$$

where  $V_0$  is the volume occupied by a segment in the fundamental state. Because it requires the formation of free volume, the transition from the fundamental to activated states leads to an increase in thermal expansivity, given by:

$$\Delta\alpha = \frac{v_0}{V_0} \frac{dP}{dT} \tag{4}$$

This transition is further accompanied by an increase in the specific heat  $\Delta C_p$ , given by:

$$\Delta C_p = \frac{Q}{M} \frac{dP}{dT} \tag{5}$$

where  $M$  denotes the molecular weight of a segment. Equation (5) can be rewritten as:

$$\Delta C_p = \frac{R}{M} \frac{dP}{d\left(\frac{RT}{Q}\right)} = \frac{R}{M} f(m, RT/Q) \tag{6}$$

We may consider that above  $T_g$ ,  $P$  is greater than 0.1 (see below) and therefore varies linearly with  $RT/Q$ , which implies that  $(M/R)\Delta C_p$  depends only on  $m$ .

In this case, equation (6) reduces to:

$$f(m) = \frac{dP}{d\left(\frac{RT}{Q}\right)} = \frac{M}{R} \Delta C_p \tag{7}$$

Thus  $f(m)$  remains constant for a given value of  $m$  and may be obtained, for example, from the graphs of Figure 1, or calculated from equations (7) and (2); the variation of this quantity as a function of  $m$  is given in Figure 2.

If the activated states correspond to flexed bonds, we may

consider (see Robertson<sup>15</sup>) that a flexed bond consists of the smallest chain segment containing two non-rigid and non-colinear bonds. If so,  $M$  can easily be evaluated for the three polymers considered here, i.e. poly(vinyl chloride) (PVC), poly(methyl methacrylate) (PMMA) and polystyrene (PS) and thus is simply equal to the molecular weight of the monomer unit.  $f(m)$  may thus be calculated from  $\Delta C_p$  using equation (7), and  $m$  may be obtained from  $f(m)$  together with the graph of Figure 2. Results are given in Table 1 and the data in Tables 1 and 2. A problem arises because of the discrepancy between the data related to  $\Delta C_p$  given in the literature (see Table 2 where two extreme values are given); this is why the values of  $m$  obtained are approximate.

For the sake of simplicity, we will continue with a given value of  $m$  lying between 10 (found for PVC) and 30 (found for PMMA and PS), say,

$$m = 20 \tag{8}$$

and which is related to the value of  $f(m)$

$$f(m) = 3.14 \tag{9}$$

Equations (8) and (9) define a given hypothetical polymer having intermediate characteristics.

We now attempt to establish that above  $T_g$  the fraction  $P$  varies linearly with  $RT/Q$ . In this respect we will not make use of the idea formulated by Williams, Landel and Ferry<sup>1</sup> that  $T_g$  is the temperature at which all the polymers reach the same value of free volume. We will depart from this concept and propose that  $T_g$  is the temperature at which all the polymers have the same fraction of activated segments (the choice of this basic assumption will be justified in the course of this paper). Let  $P_{T_g}$  be this fraction. Boyer<sup>16</sup> formerly evaluated the fraction of holes at  $T_g$  by various methods. This quantity equals  $P_{T_g}$  since Boyer considered that free

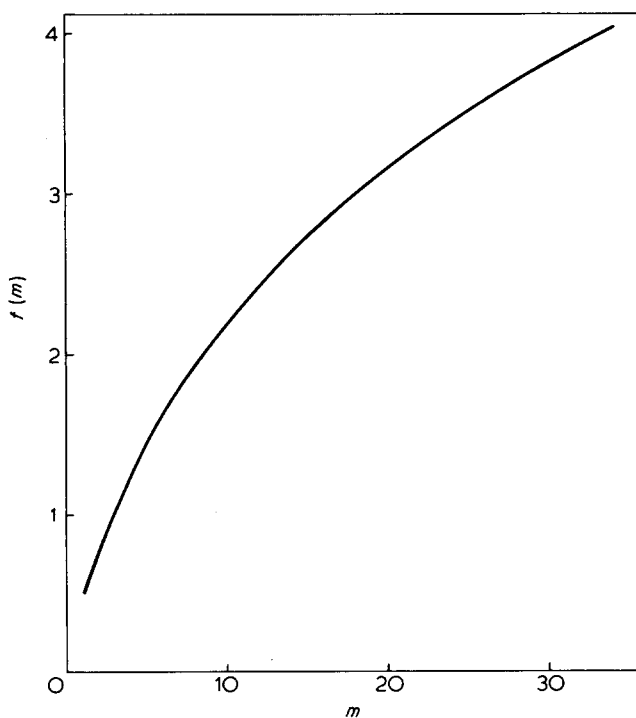


Figure 2 Calculated value of  $f(m)$  as a function of  $m$ , using equations (2) and (7)

Table 1 Characteristic quantities and adjustable parameters implied by the model

Polymer	$M$ (g mol <sup>-1</sup> )	$\rho$ (g cm <sup>-3</sup> )	$V_0 = M/\rho$ (cm <sup>3</sup> )	Adjustable parameters				
				$m$	$Q$ (kcal)	$v_0$ (cm <sup>3</sup> )	$v_i$ (cm <sup>3</sup> )	$p_0$ (kg mm <sup>-2</sup> )
PS	104	1.03	101	30	3.95	16.15	10.82	6
PVC	62.5	1.39	45	10	3.00	11.50	5.00	11
PMMA	101	1.18	86	30	4.10	14.40	8.20	19

Table 2 Experimental data required to test the model

Polymer	$\Delta C_p \times 10^2$ (cal g <sup>-1</sup> C <sup>-1</sup> )		$T_g$ (°C)		$\Delta\alpha \times 10^4$ (atm. pressure)	$\Delta\alpha \times 10^4$ $p = 10$ kg mm <sup>2</sup> Data	$\beta \times 10^3$ $g_2$ (mm <sup>2</sup> kg <sup>-1</sup> ) Data
	Data	Adopted	Data	Adopted			
PS	7.1 <sup>9</sup>	7.3	80 <sup>6</sup>	92.5	3.08 <sup>6</sup>	2.29 <sup>6</sup>	—
	7.9 <sup>16</sup>		100 <sup>16</sup>				
PVC	6.8 <sup>9</sup>	7.0	75 <sup>7</sup>	75.5	3.71 <sup>7</sup>	2.60 <sup>7</sup>	2.5 <sup>7</sup>
	7.5 <sup>16</sup>		77 <sup>16</sup>				
PMMA	7.0 <sup>9</sup>	7.5	103 <sup>7</sup>	106.5	3.10 <sup>7</sup>	2.52 <sup>7</sup>	3 <sup>7</sup>
	8.17 <sup>16</sup>		105 <sup>16</sup>				

volume consists of holes. His results were found to be in good agreement for PS ( $P_{T_g} = 0.111$ ) and PMMA ( $P_{T_g} = 0.124$ ). We will adopt an intermediate value:

$$P_{T_g} = 0.118 \quad (10)$$

As this value is higher than 0.1, it follows that above  $T_g$  a linear dependence of  $P$  on  $RT/Q$  may be considered (see Figure 1). Thus  $f(m)$  and  $m$  may be estimated provided the proposed definition of  $T_g$  is accepted.

For  $T = T_g$ , equations (2), (8) and (10) give:

$$Q/RT_g = 2 + \ln m \cong 5 \quad (11)$$

Equation (11) allows the calculation of  $Q$  from  $T_g$ , and we can rewrite equation (2) as:

$$P = \frac{\exp(3 - 5T_g/T)}{1 + \exp(3 - 5T_g/T)} \quad (12)$$

The curve calculated from (12) is given in Figure 3. Moreover, we are now able to give an interpretation of the following empirical relations previously given by Simha and Boyer<sup>14</sup>, i.e.:

$$\Delta C_p T_g = 25 \text{ cal} \quad (13)$$

and

$$\Delta\alpha T_g = 0.113 \quad (14)$$

These may be obtained from equations (7), (9) and (11) and from equations (4), (5), (13), respectively, assuming that:

$$Q/M = 40 \text{ cal} \quad (15)$$

and

$$v_0/V_0 = 0.18 \quad (16)$$

Equations (15) and (16) lead to the conclusion that the energy  $Q$  and the free volume  $v_0$  are proportional to the molecular weight and the volume of a segment respectively, which seems reasonable. Equations (8), (15) and (16) give constant values only for quantities which depend on the chemical nature of the segment and may vary from one polymer to another, but equation (10) must hold for all the polymers.

#### EFFECT OF PRESSURE ON SPECIFIC VOLUME

To account for the effect of pressure on free volume above  $T_g$ , we will make a further assumption. We suppose that  $v_0$  (the free volume associated with an activated segment) is composed of  $v_i$ , an incompressible part related to the local configuration which is less compact because of the local lack of regularity, and  $v_c$  a compressible part. Let us assume that the application of a hydrostatic pressure  $p$  entails a decrease of  $v_0$  and therefore of  $v_c$  only.

We will adopt the simplest law which fulfils the following conditions:

$$\left. \begin{aligned} v_c &= 0 \text{ when } p = \infty \\ \text{and} \\ v &= v_{c0} \text{ when } p = 0 \end{aligned} \right\} \quad (17)$$

The perfect gas law is suitable:

$$(p + p_0)v_{cp} = p_0 v_{c0} \quad (18)$$

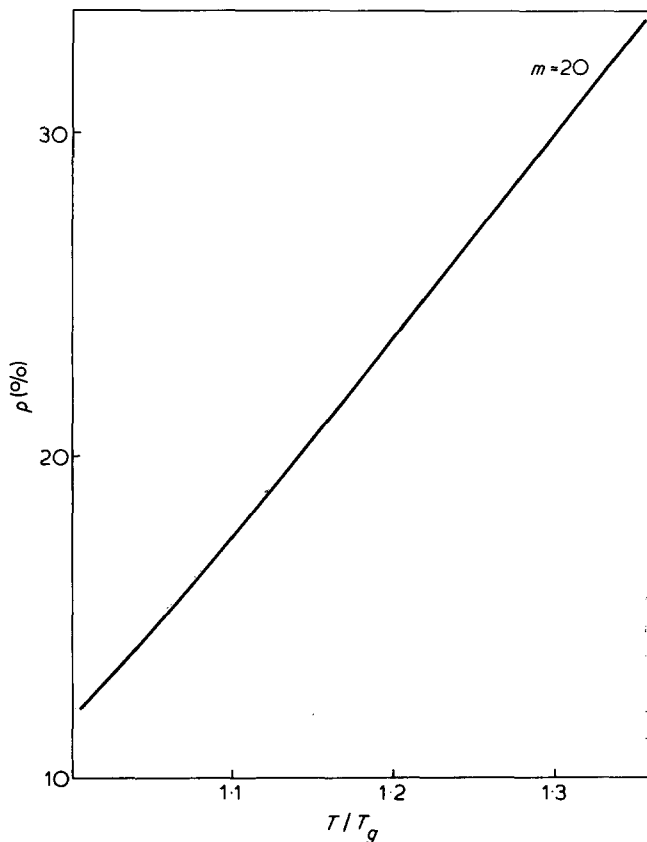


Figure 3 Fraction of activated segments as a function of reduced temperature  $T/T_g$ , calculated from equation (12)

where  $v_{cp}$  denotes the value of  $v_c$  at a pressure  $p$ , and  $p_0$  denotes an internal pressure. The physical meaning of this last quantity is probably related to cohesive forces.

At constant pressure when a segment jumps from the fundamental to an activated state, it does mechanical work against the pressure. This work satisfies the following relation:

$$(p_0 + p)(v_i + v_{cp}) = p_0 v_0 + p v_i \quad (19)$$

Therefore, when a polymer is compressed, it requires an increase of energy:

$$\Delta Q = p v_i \quad (20)$$

where  $p_0 v_0$  is absorbed by  $Q$ . In this case, taking into account equations (19) and (20), equations (2) and (4) become, respectively:

$$P_p = \frac{m \exp[-(1/RT)(Q + p v_i)]}{1 + m \exp[-(1/RT)(Q + p v_i)]} \quad (21)$$

and

$$\Delta \alpha_p = \frac{p_0 v_0 + p v_i}{V_0(p_0 + p)} \frac{dP_p}{dT} \quad (22)$$

where the subscript  $p$  indicates that the quantity considered is related to a pressure  $p$ .

We intend to test equation (22) using literature data. Hellwege *et al.*<sup>6</sup> have performed dilatometric experiments over a wide range of temperatures in order to measure the

pressure effects on thermal expansivity. Their most accurate results were obtained on PS; these are shown in Figure 4 as points superimposed on a theoretical curve (full line). This curve is, in graphical form, a numerical solution of equation (22) calculated as follows. Values of  $m$ ,  $Q$  and  $v_0$  for PS are obtained from equations (7), (10) and (4); these are listed in Table 1. However,  $p_0$  and  $v_i$  are not known. A possible determination is to adjust these quantities in order to obtain the best agreement between the response of equation (22) and the data of Figure 4. The shape of the curve is found to be reasonable and the optimized values of  $p_0$  and  $v_i$  given in Table 1, seem to be acceptable.

It follows from our proposed definition of  $T_g$  that this temperature must change when the polymer is compressed. At  $T_g$ ,  $P_p$  must still equal the value given by equation (10) and thus we find from equation (21):

$$\frac{Q}{RT_{g0}} = \frac{Q + p v_i}{RT_{gp}} \quad (23)$$

where  $T_{g0}$  denotes the value of  $T_g$  at atmospheric pressure. This last equation allows for hydrostatic pressure effects on  $T_g$  to be calculated.

Using Tables 1 and 2, we have found that for PS:

$$\frac{dT_g}{dp} = 2.4^\circ\text{C/kg mm}^{-2} \quad (24)$$

which must be compared with the value of  $3.3^\circ\text{C/kg.mm}^{-2}$  given by Hellwege *et al.*<sup>6</sup>. This latter value is probably too large because it is estimated from isothermal and not from isobaric measurements.

Let us recall the distinction between both types of measurement and refer to Figure 5 where the specific volume is shown schematically versus temperature. We consider a temperature  $T_x$ , sufficiently above  $T_g$  that the polymer would be in equilibrium, and another temperature  $T_y$ , sufficiently below  $T_g$  that the polymer would be in the glassy state. An isobar is drawn for a polymer which is cooled from  $T_x$  to  $T_y$  at constant applied hydrostatic pressure  $p$  (sequence ABCD); an isothermal measurement of the specific volume is obtained on cooling the polymer from  $T_x$

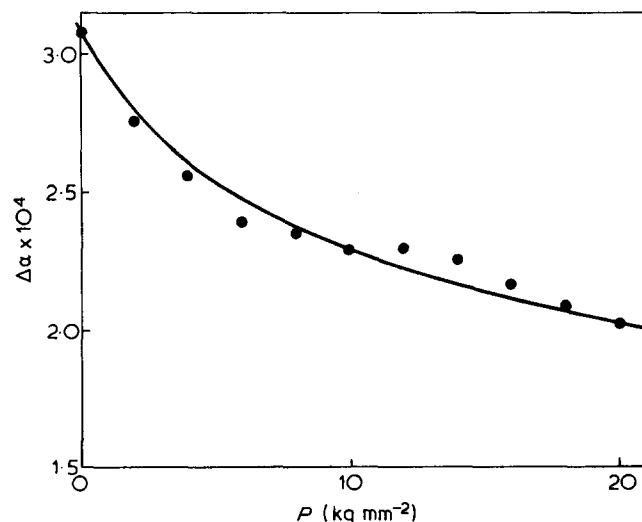


Figure 4 Thermal expansivity of PS as a function of hydrostatic pressure. Points: ●, data of Hellwege *et al.*<sup>6</sup>; calculated from equation (22) using values given in Table 1

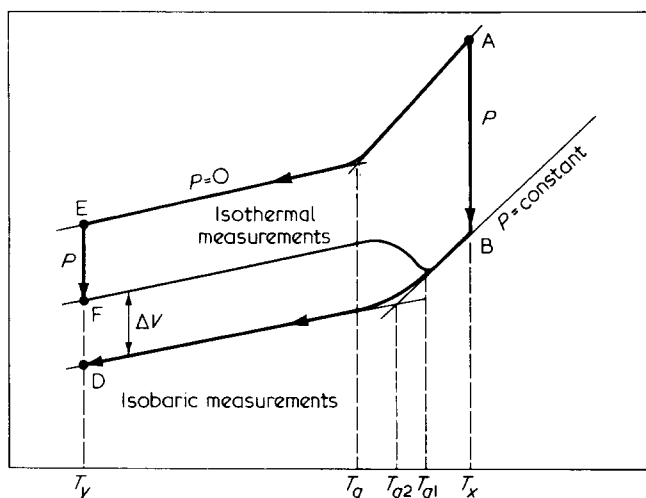


Figure 5 Specific volume as a function of temperature deduced from isothermal and isobaric measurements (schematic)

to  $T_y$  at  $p = 0$  and then applying  $p$  at  $T_y$  (sequence AEF).

It can be seen from the graph that the transition temperature  $T_{g1}$  related to isothermal measurements at a pressure  $p$ , is higher than  $T_{g2}$  obtained from the isobar related to the same pressure (of course both temperatures superimpose at atmospheric pressure). The lowest temperature at which the equilibrium can be attained quickly is located just above  $T_{g1}$ , where both types of measurements merge.

Heydemann and Guicking<sup>7</sup> obtained the temperature dependence of the specific volume from isothermal and isobaric measurements for PVC and PMMA. Their values of  $dT_g/dp$  determined from isobaric measurements are given in Table 3. The theoretical evaluation of this quantity requires a knowledge of  $v_i$  (see equation 33). If we make use of numerous accurate data for  $\Delta\alpha_p$  as a function of  $p$ , values of  $p_0$  and  $v_i$  may be adjusted to give the best fit to the data (we have adopted this procedure for case of PS). Unfortunately, there are few such data for PVC and PMMA, because the measurements carried out by Heydemann and Guicking do not cover an extended range of temperatures and pressures; thus equation (33) and experimental values of  $dT_g/dp$  cannot be checked and these values will only be used to determine  $v_i$  from equation (33). These authors compare isothermal and isobaric measurements, permitting us to test our model from other data, namely, the differences in the specific volume found from both types of measurements over the glassy range.

We calculate such a difference and return to Figure 5. At  $T_x$ , when the polymer is compressed from A to B in an equilibrium state, the free volume associated with the activated segments decreases according to equation (18). From B to C, as the polymer is cooled at constant pressure  $p$ , the free volume decreases, because the fraction of activated segments decreases to reach a value of 0.118 at  $T_{g2}$  (equation 10). Below this temperature the molecular motions are frozen in and the fraction of activated segments may be considered to equal 0.118 and to remain constant in a non-equilibrium state — the glassy state.

However from E to F, at  $T_y$  the polymer is compressed in the glassy state, the free volume cannot reach its equilibrium value and its compressibility does not differ from that of the polymer itself. It follows that the decrease in the specific volume is far smaller from E to F than from A to B. Thus the specific volume of a polymer is higher at F than at D, although both states are related to the same temperature

and pressure and, in our opinion, the same value of  $P = 0.118$ .

Let  $v_{01}$  be the value of  $v_0$  related to F, expressed by:

$$v_{01} = v_0(1 - \beta_g p) \quad (25)$$

where  $\beta_g$  denotes the compressibility factor in the glassy state.

Let  $v_{02}$  be the value of  $v_0$  related to D; this value does not differ from that related to C and therefore can be evaluated from equation (19):

$$v_{02} = \frac{p_0 v_0 + p v_i}{p_0 + p} \quad (26)$$

Below  $T_{g1}$ , a difference  $\Delta v$  exists between values of the specific volume determined at a given pressure and temperature from isothermal and isobaric measurements. If we assume that in both cases the fraction of activated segments equals  $P_{T_g}$ , the expression from  $\Delta v$  may be obtained from equations (25), (26) and (10):

$$\Delta v = (V/V_0)(v_{01} - v_{02})P_{T_g} = 0.118 (V/V_0)(v_{01} - v_{02}) \quad (27)$$

where  $V$  denotes the specific volume in the glassy range at atmospheric pressure.

Thus, it can be seen from the proposed model, that the relative difference in the specific volume  $\Delta v/V$  depends on five parameters:  $m$ ,  $Q$ ,  $v_0$ ,  $v_i$  and  $p_0$ . For PVC and PMMA, the five parameters were calculated from equation (7), (10), (4), (23) and (22) using experimental values of  $\Delta C_p$ ,  $T_g$ ,  $\Delta\alpha$ ,  $dT_g/dp$  and  $\Delta\alpha_p$ , respectively. Results and data are collected in Tables 1, 2 and 3. Now that all the required parameters are determined, no further adjustments need be made to calculate  $\Delta v/V$  for PVC and PMMA from equations (25), (26) and (27). Therefore a good agreement between calculated and experimental values of  $\Delta v/V$  constitutes a check on the model. Results and given and compared in Table 3, and fairly good agreement is observed, although there is some difference between the two polymers.

#### ELEMENTARY PROCESS OF PLASTIC DEFORMATION IN THE GLASSY STATE

We have previously established a temperature, strain rate and pressure-dependent yield criterion<sup>17</sup>, which may be simply expressed by:

Table 3 Comparison between experimental and calculated values of  $dT_g/dp$  and  $\Delta v/V$

Polymer	$dT_g/dp$ (°C/kg mm <sup>-2</sup> )		$\Delta v/V$ (at $p = 10$ kg/mm <sup>2</sup> )	
	Data	calc. from (23)	Data	calc. from (27)
PS	3.36*	2.4	—	—
PVC	1.4 <sup>7</sup>	—	$(7 \pm 0.4) \times 10^{-3}$	$7.3 \times 10^{-3}$
PMMA	1.8 <sup>7</sup>	—	$(2.4 \pm 0.2) \times 10^{-3}$	$2.4 \times 10^{-3}$

\* Probably too large (see text)

Table 4 Values of the constants characterizing the plastic deformation process (theoretical values are calculated for  $n = 25$ )

Polymer	$Q_0$ (kcal)		-Log 2C (C in s)		A ( $10^{-4}$ kg mm $^{-2}$ ) exp.	$\epsilon_0$ calc.	$\mu$ exp.	$\Delta V_0/v_0$ calc.
	exp.	calc.	exp.	calc.				
PVC	70.5 <sup>11</sup>	75	38 <sup>11</sup>	38	7 <sup>11</sup>	1.06	0.13 <sup>17</sup>	1.14
PMMA	98.5 <sup>21</sup>	102.5	51 <sup>21</sup>	50	5.5 <sup>21</sup>	0.71	0.18 <sup>21</sup>	1.41

$$\tau_{\text{oct}} + \mu p = f(\dot{\epsilon}, T) \quad (27)$$

where  $\tau_{\text{oct}}$  denotes the octahedral shear stress, first introduced by Nadai<sup>18</sup> and  $\dot{\epsilon}$  the strain-rate,  $\mu$  is a constant, the physical meaning of which has been proposed in a previous paper<sup>19</sup>. In parallel with this criterion, we describe<sup>20</sup> the yield behaviour by an Eyring-type equation<sup>13</sup> derived from the theory of activated processes, which can be rewritten as:

$$\ln \dot{\epsilon} = \frac{\sigma - [3/(2)^{1/2}] \mu p}{AT} - \ln 2C + Q_0/RT \quad (28)$$

where  $\sigma$  is the tensile yield stress,  $A$  and  $C$  are constants and  $Q_0$  denotes the activation energy of the yield process.

Equation (28) has been successfully tested over an extended range of temperatures and strain rates<sup>10-12,21</sup> for at least three glassy polymers. We believe that the formalism is suitable, but the constants  $A$  and  $C$  still need to be explained as a function of the segmental motion leading to the plastic deformation. Of course, the activation theory of plastic deformation implies that  $A$  and  $C$  are related respectively to the activation volume and the jump frequency but these quantities have not yet been estimated or checked satisfactorily. This model overcomes this difficulty.

We start from the assumption that the molecular origin of the yield process consists of a change of configuration. To produce this,  $n$  segments must be activated simultaneously. When no stress is applied, the frequency of such an event is given by:

$$\nu = \frac{2kT}{h} [m \exp(-Q/RT)]^n \quad (29)$$

where  $kT/h$  denotes the Debye frequency factor and  $k$  and  $h$  the Boltzmann and Planck constant, respectively, (the reason for using the same parameter  $Q$  as in equation (2) will be given in the discussion). When a stress  $\sigma$  is applied, the change of configuration gives rise to the deformation  $\epsilon_0$  of volume  $nV_0$ . The work done by this stress is:

$$W_\sigma = nV_0 \epsilon_0 \sigma \quad (30)$$

According to the Eyring theory, the strain-rate  $\dot{\epsilon}$  may be expressed from equations (20) and (30) by:

$$\dot{\epsilon} = \epsilon_0 \frac{kT}{h} m^n \exp - \frac{n(Q - \epsilon_0 V_0 \sigma)}{RT} \quad (31)$$

which can be rewritten as:

$$\ln \dot{\epsilon} = \ln \frac{kT}{h} \epsilon_0 + n \ln m - \frac{nQ}{RT} + \frac{n \epsilon_0 V_0 \sigma}{RT} \quad (32)$$

When the hydrostatic  $p$  is applied, equation (32) becomes:

$$\ln \epsilon = \ln \frac{kT}{h} \epsilon_0 + n \ln m - \frac{nQ}{RT} + \frac{n \epsilon_0 V_0 \sigma}{RT} - \frac{np \Delta V_0}{RT} \quad (33)$$

where  $\Delta V_0$  denotes the volume increase required to activate a segment at a pressure  $p$  when a stress  $\sigma$  is acting. It follows that  $\Delta V_0$  must be at least equal  $v_0$ .

Equation (33) must be compared with equation (28) which characterizes the strain rate at yield from a macroscopic point of view. The quantities  $Q_0$ ,  $C$ ,  $A$  and  $\mu$  can now be identified as:

$$Q_0 = nQ \quad (34)$$

$$C = \frac{kT \epsilon_0 m^n}{2h} \quad (35)$$

$$A = \frac{R}{n \epsilon_0 V_0} \quad (36)$$

$$\mu = \frac{(2)^{1/2} \Delta V_0}{3 \epsilon_0 V_0} \quad (37)$$

For PVC and PMMA, experimental values of these four quantities are known from our previous work<sup>11,20</sup> and recorded in Table 4. The theoretical evaluation of  $Q_0$  and  $C$  using equations (34) and (35) and some of the characteristics given in Table 1 requires knowledge the value of  $n$  (i.e. the number of activated segments giving rise to the plastic deformation process). This number has been adjusted in order to obtain the best fit between experimental and calculated values of  $Q_0$ ,  $C$  and  $A$ , keeping in mind that  $\epsilon_0$  must approach unity. The value

$$n = 25 \quad (38)$$

was finally chosen. This value agrees with the volume relaxation environment of 26 monomer units proposed by Robertson<sup>22</sup> in a treatment based on theoretical considerations.  $\epsilon_0$  was then evaluated from equations (36) and (38) and the experimental value of  $A$ . Results are given in Table 4. As expected the values approach unity.  $Q_0$  and  $C$  are calculated from equations (34), (35) and (38) and collected in Table 4.

Experimental values of  $\mu$  allow calculation of  $\Delta V_0$  using equation (37), and  $\Delta V_0/v_0$  given in Table 4: this ratio is found to be slightly greater than unity, which is plausible.

## DISCUSSION

The model accounts for thermodynamic properties as well as the yield deformation of glassy polymers. However, this

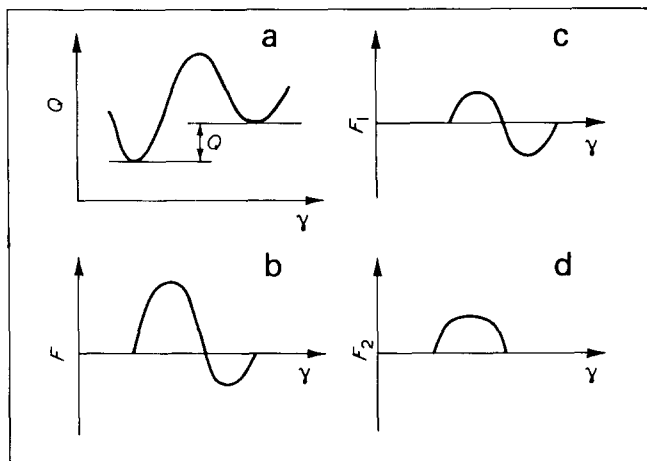


Figure 6 Schematic variation of the energy barrier (Figure 6a) and the cohesive force  $F$  (Figure 6b) related to a segment as a function of  $\gamma$ .  $F_1$  and  $F_2$  are the components of  $F$  (Figures 6c and 6d)

model is an approximation because it deals only with average values of the quantities considered, although it considers amorphous materials known to have local structure which is not uniform and, moreover, depends on aging and thermal history. This implies that in the glassy state, some of the parameters such as  $m$  and  $Q$  must be replaced by distribution functions which may be modified during thermal treatment.

This model is not applicable either to deformation processes taking place above  $T_g$ , because these processes are probably not related to activated segments but to the diffusion of the free volume present in the polymer.

Returning to the proposed definition of  $T_g$ , we point out that this implies equal segmental mobility for all polymers at this temperature. Indeed, from equations (29) and (38), the frequency at which the configurations change at  $T_g$  is given by:

$$v_{T_g} = \frac{2kT_g}{h} m^{25} \exp - \frac{25Q}{RT_g} \quad (39)$$

and maintains a quasi-constant value providing  $PT_g$  is the same for all polymers as assumed here.

The concept that  $T_g$  corresponds to a universal value of segmental mobility is generally accepted in the literature.

Finally, we have to justify the use of the same parameter  $Q$  for the mean increase in energy of an activated segment (equation 2) and for the activation energy related to the rate process (equation 29). We assume that the change of configuration which characterizes the rate process requires the simultaneous activation of  $n$  segments. Let  $\gamma$  denote the elementary deformation involved in such a process. The cohesive force resulting from this deformation is the sum of the forces related to each segment. Let  $F$  be the force acting on one segment. It derives from an asymmetric energy barrier. The variation of both quantities versus  $\gamma$  is schematically

represented in Figure 6 (a and b).  $F$  may be considered to be composed to two components:  $F_1$ , a force deriving from a symmetrical energy barrier, having a positive and negative symmetrical variation versus  $\gamma$  (see Figure 6c) and  $F_2$  a force which always remains positive (see Figure 6d). The sum of the components  $F_1$  related to the  $n$  segments is statistically low in any state of the deformation, because it is highly improbable that the energy barriers of the  $n$  segments are surmounted in phase. Thus the contribution may be neglected and only the sum of the  $F_2$  components (always positive) has to be taken into account. The energy related to  $F_2$ , (area under curve Figure 6d) is  $Q$ , the difference in the energy barriers related to the ground and activated states, respectively. This is why the mean activation energy characterizing the rate process for plastic deformation equals  $nQ$  (equation 29).

## CONCLUSIONS

(1) The formation of free volume and the molecular motions giving rise to plastic deformation in the glassy state arise from the same process. It implies the transition of segments from fundamental to activated states, the length of these segments being about one monomer unit.

(2) Plastic deformation in the glassy state requires the cooperative motion of about 25 segments.

(3) The glass transition temperature corresponds to a constant fraction of activated segments and not to a constant value of free volume.

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