

## Internal Stresses and Activation Volumes from the Stress Relaxation Behavior of Polyethylene at Low Deformations

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### Synopsis

Internal stress levels and values of the activation volume have been evaluated from the kinetics of stress relaxation in annealed samples of LD and HD polyethylene. The initial deformation of the samples was varied, the maximum values amounting to ca. 1%. The temperature of the experiments was 24°C for LDPE, and 24°, 50°, and 69°C for HDPE. The internal stress level was found to be approximately proportional to the initial deformation and independent of the temperature used. Such internal stresses appear to be introduced upon deformation, since permanent stresses had been removed by careful annealing. The activation volume ( $v$ ) was found to satisfy the relation  $v\sigma^* \approx 10kT$ , where  $\sigma^*$  is the effective stress, i.e., the difference between the applied and internal stress,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature. This is in good agreement with results reported elsewhere for a wide variety of materials. This relation applies primarily to the exponential flow portion of the relaxation curves, but by a simple transformation the power-law region can also be encompassed.

### INTRODUCTION

It is well known that the analytical tools used for the description of flow in polymers and metals differ greatly. Flow measurements in metals are normally described in terms of the hypothesis of stress-aided thermal activation,<sup>1,2</sup> whereas corresponding data for polymers are generally described as resulting from relaxation or retardation time spectra.<sup>3</sup> With regard to stress relaxation, the variation of stress with time is often of the  $\log t$  type. Such a time dependence corresponds, at least formally, either to an activation energy linearly diminishing with the applied stress or to a broad (box) distribution of relaxation times. Quite naturally, comparisons between materials of different structure and composition are rare, although the literature gives a number of indications of certain basic similarities when comparing, for instance, metals and amorphous and semicrystalline polymers.<sup>4-6</sup>

The present paper aims at presenting experimental results concerning the stress relaxation behavior of polyethylene in the low-deformation region, analyzed in terms of the theory of stress-aided thermal activation. Special interest is devoted to the concept of the activation volume and its stress dependence. With regard to stress, the role of internal stresses is analyzed using different methods for their determination. The analysis starts from the well-

known fact that the relaxation process consists of two regions, characterized by an exponential and a power-type dependence of the flow rate on stress. The transition between these two regions is found useful as a means for normalizing the stress dependence of the activation volume. It will be shown that this dependence conforms quantitatively with known data for other polymers and metals,<sup>2,4,7,8</sup> provided that the influence of internal stresses is accounted for.

## THEORETICAL BACKGROUND

### Stress-Aided Thermal Activation

The idea of stress-aided thermal activation is based on the following expression:<sup>1,2</sup>

$$\dot{\sigma} = -A \exp(-\Delta G/kT) \quad (1)$$

where  $\dot{\sigma}$  is the relaxation rate  $d\sigma/dt$ , with  $\sigma$  denoting the stress;  $\Delta G$  is the free energy of activation assumed to depend linearly on  $\sigma$ ;  $k$  is Boltzmann's constant;  $T$  is the temperature; and  $A$  is a constant (preexponential) factor. Assuming that the mobile entities, as, for instance, dislocations, can cross the potential barrier in the reverse direction as well, the exponential term in eq. (1) has to be replaced by  $\sinh(-\Delta G/kT)^2$ .

### The Activation Volume

From the stress dependence of the stress rate, the activation volume  $v$  can be calculated. One then obtains<sup>2</sup>

$$v = - \left( \frac{\partial \Delta G}{\partial \sigma^*} \right)_{T,p} = kT \left( \frac{\partial \ln \dot{\sigma}}{\partial \sigma^*} \right)_{T,p} \quad (2)$$

where  $\sigma^*$  is the effective stress, i.e., the difference between the applied ( $\sigma$ ) and the internal ( $\sigma_i$ ) stress; and  $p$  is the hydrostatic pressure. Provided  $v$  has a constant value,  $\Delta G$  decreases linearly with the effective stress, the resulting relaxation rate being given by

$$\dot{\sigma} = -A' \exp(v\sigma^*/kT) \quad (3)$$

where  $A'$  is assumed to be independent of stress. Similar expressions apply also to secondary creep.

Equation (3) is the normal base for analyzing flow in metals and other crystalline solids.<sup>2</sup> The number of papers utilizing this expression for an analysis of the flow in polymers is rather small.<sup>4,6,8-10</sup>

It is known that, for both polymers and metals, a stress relaxation curve plotted in a  $\sigma(\log t)$  diagram consists of two parts.<sup>11,12</sup> First, there is a linear part at shorter times, where the stress is linear with  $\log t$ . This part is described by eq. (3), as  $\dot{\sigma} \sim \exp \sigma^*$  is equivalent to  $\sigma \sim \log t$ . The second part is linear in the  $\log \sigma^*$  ( $\log t$ ) plot; it can be described by a power-type expression of the following form:<sup>13,14</sup>

$$\dot{\sigma} = -B(\sigma^*)^n \quad (4)$$

where the parameters  $B$  and  $n$  are stress independent. Equation (4) is known as the power law of flow. Using eq. (2), the value of  $v$  becomes<sup>11</sup>

$$v = kT n / \sigma^* \quad (5)$$

Within the power-law region, the activation volume consequently changes with the actual stress during a relaxation experiment. Contrary to this, the value of  $v$ , within the exponential-law region, depends only on the initial stress  $\sigma_0$  of the relaxation curve, provided  $T$  is constant.<sup>4</sup> A convenient method of calculating  $v$  is to take the slope of the linear  $\sigma(\log t)$  portion, which equals  $F = kT/v$ .<sup>11</sup>

It has been found<sup>4</sup> that for solids of widely differing structure and composition, the following relation applies:

$$v \sigma_0^* = 10kT \quad (6)$$

It is important to note that  $\sigma_0^*$  denotes the dissipated stress and not the initial stress. In certain materials,  $\sigma_0$  and  $\sigma_0^*$  may be equal; in others,  $\sigma_0$  has to be corrected for the stress  $\sigma_\infty$  remaining after infinite time,  $\sigma_0^*$  being equal to  $\sigma_0 - \sigma_\infty$ .

### The Transition Stress Between the Exponential and Power-Law Regions

If the stress relaxation curves and their first two derivatives are continuous, there must exist a stress value demarcating the transition from the exponential to the power-law region, according to eqs. (5) and (6), respectively. This transition stress  $\sigma_{tr}$  is<sup>7</sup>

$$(\sigma_{tr} - \sigma_i) / (\sigma_0 - \sigma_i) = n/10 \quad (7)$$

The validity of eq. (7) has been confirmed for both polymers and metals.<sup>7</sup> Equation (7) implies that  $v$  is constant in the region  $\sigma_0 \rightarrow \sigma_{tr}$ , while it varies in inverse proportion to  $\sigma$  at stresses lower than  $\sigma_{tr}$ .

### The Determination of Internal Stresses

Apparently, as internal stresses enter the effective stress, which in turn governs the kinetics of flow, it is natural to design methods for the determination of  $\sigma_i$  which are based on an analysis of flow curves. Various kinds of internal stresses and how to measure and distinguish between them are discussed in detail below.

## EXPERIMENTAL

### Samples

The following grades of polyethylene were used:

**HDPE.** Lupolen 6011 L (BASF), density 0.960–0.963 g/cm<sup>3</sup>, melt index 4.0–6.0 g/10 min (MFI 190/2).

**LDPE.** Union Carbide DFD 4400 (DYNH type), density 0.920 g/cm<sup>3</sup>, melt index 2.0 g/10 min (MFI 190/2),  $M_v = 9 \times 10^4$ .

Samples of HDPE and LDPE (dimensions  $0.5 \times 5 \times 50$  mm) were produced by compression molding ( $165^\circ\text{C}$ , 0.5 MPa, 3 hr). The specimens were annealed for 12 hr (HDPE at  $120^\circ\text{C}$ , LDPE at  $80^\circ\text{C}$ ) to eliminate residual stresses.

### Method

The device used for the stress relaxation measurements has been described earlier.<sup>15</sup> The experiments were conducted mainly at room temperature ( $24^\circ\text{C}$ ); but with HDPE, also  $50^\circ$  and  $69^\circ \pm 0.2^\circ\text{C}$  were used. The maximum deformation of the samples was about 1%.

## RESULTS

### The Two Regions of Flow in Stress Relaxation

As pointed out above, the relaxation process can be divided into two regions, the exponential-law (shorter times) and the power-law regions (longer times). Figure 1 shows a typical example of this behavior illustrated with results obtained on LDPE and HDPE at  $24^\circ\text{C}$ . It can be seen that at an initial stress of 13.9 MPa for HDPE and 1.07 MPa for LDPE (strains 0.80% and 0.49%, respectively), the transition between the two regions of flow occurs after approximately 30 sec.

The latter portion of the curves shown in Figure 1 obeys the power law, eq. (4), as evident from the double logarithmic representation in Figure 2. This is true of both LDPE and HDPE used here, i.e., compression-molded, isotropic samples. Earlier, similar results were obtained with highly oriented PE samples (extension ratio 6).<sup>12</sup>

With regard to metals, it has been discussed at considerable length to what extent the two regimes of flow are related.<sup>16</sup> We will now show that the exponential and power-law portions have, at least formally, a common origin.

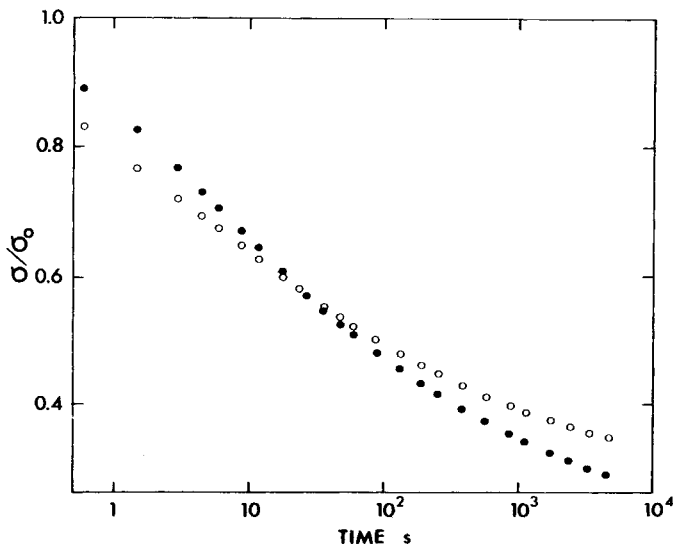


Fig. 1. Stress relaxation curves for (●) HDPE and (○) LDPE at room temperature as  $\sigma(\log t)$  plots. Initial stress, 13.9 MPa and 1.07 MPa, respectively; strain rate,  $1.4 \times 10^{-2} \text{ sec}^{-1}$ .

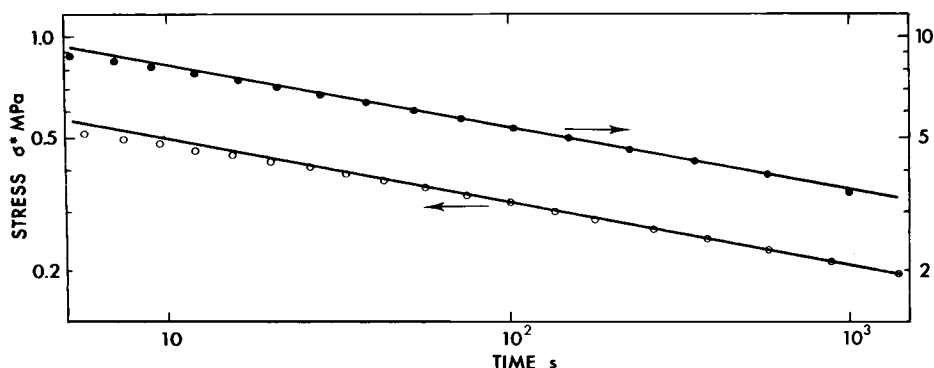


Fig. 2. Log-log representation of effective stress vs. time of the curves shown in Fig. 1.

### Internal Stresses

The whole concept of internal stress and its role in influencing the flow of solids is not especially well understood. It may, therefore, be useful to consider some basic facts first.

Figure 3 shows an example of stress relaxation curves obtained with low-density polyethylene. As can be seen, the stress does not diminish to zero but reaches a certain level, denoted  $\sigma_{\infty}$ , in the limit of long measuring times. Now, the  $\sigma_{\infty}$  value has a direct bearing on the internal stress;  $\sigma_{\infty}$  is simply equal to the internal stress value  $\sigma_i$  entering eq. (4). When the actual stress  $\sigma$  falls down to the value  $\sigma_i$ , the effective stress  $\sigma - \sigma_i$  becomes zero and the flow ceases. This obviously happens when  $\sigma$  falls to the equilibrium value  $\sigma_{\infty}$ .

Generally, the following two types of internal stresses may play a role in the present context: (a) internal stresses introduced by deforming the sample ( $\sigma_{id}$ ) and (b) residual internal stresses present in the virgin sample due to processing conditions etc. ( $\sigma_{ir}$ ).

Internal stresses induced by a deformation may be assumed to increase with the stress (deformation) applied to the sample, while stresses of the lat-

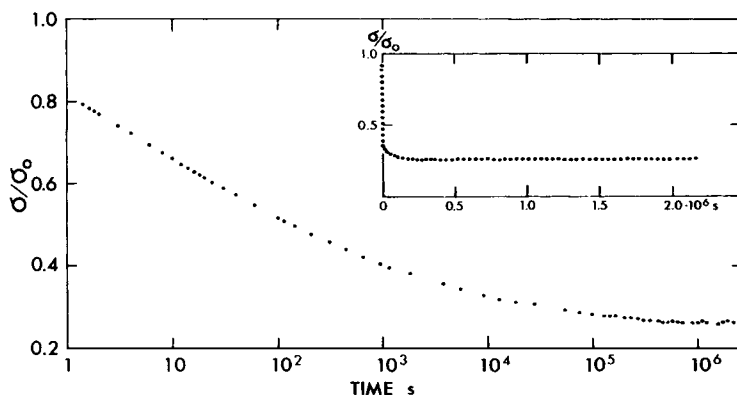


Fig. 3. Stress vs. log time and stress vs. time for LDPE at room temperature, showing the significance of the equilibrium stress  $\sigma_{\infty}$ . Initial stress, 1.73 MPa; strain rate,  $5 \times 10^{-3} \text{ sec}^{-1}$ .

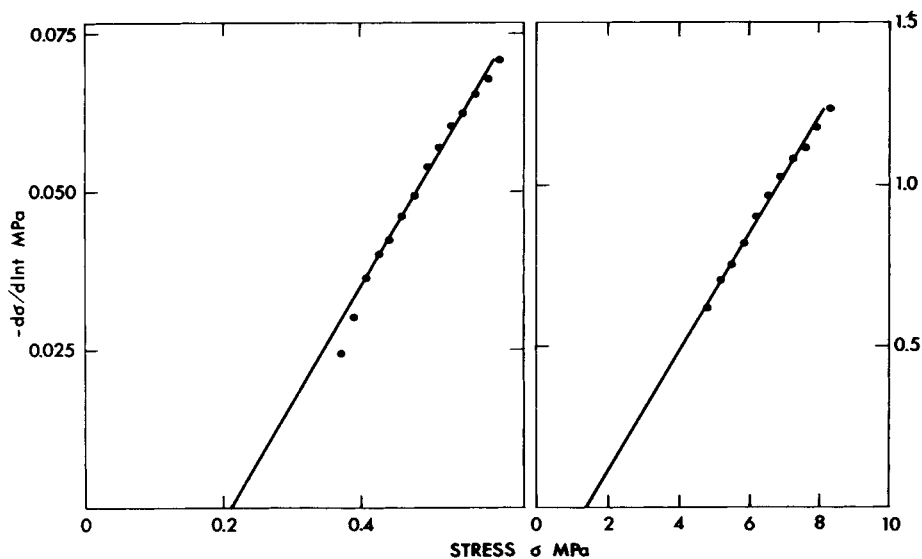


Fig. 4. Determination of the internal stress level according to Li from the relaxation curves shown in Fig. 1, for LDPE (left) and HDPE (right).

ter type, i.e., stresses remaining after processing, are likely to remain constant. This distinction does not include a possible interplay between the two types of internal stress.

For determining the internal stress level, the method illustrated in Figure 3, that is, the measurement of the equilibrium stress  $\sigma_{\infty}$ , can hardly be employed in normal practice due to the long measuring times involved. There are, on the other hand, methods where the  $\sigma_i$  level can be determined from the course of the initial part of a stress relaxation curve. Li<sup>13</sup> has suggested a method where the slope of the  $\sigma(\log t)$  curve is determined at different stress values, whereafter the slope is plotted versus the stress. The intercept of the

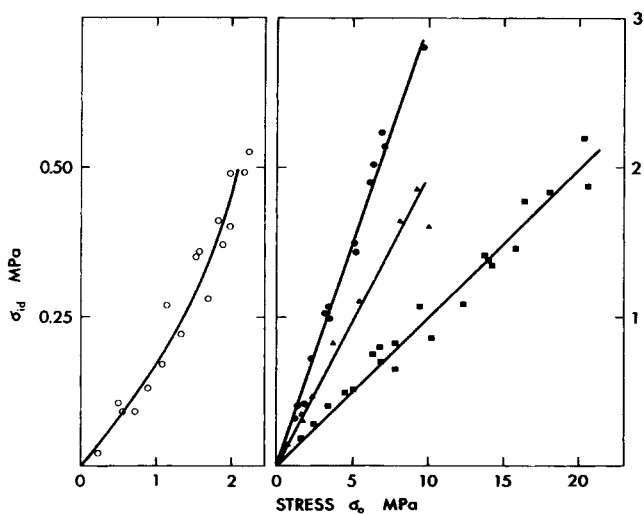


Fig. 5. Induced internal stresses  $\sigma_{id}$  vs. initial stress  $\sigma_0$  for (O) LDPE at 24°C (left) and HDPE at (■) 24°C, (▲) 50°C, and (●) 69°C (right).

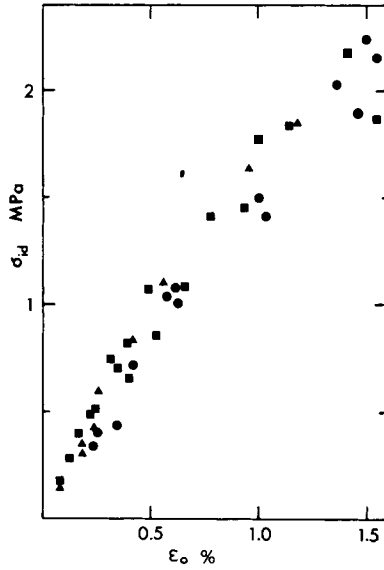


Fig. 6. Induced internal stresses  $\sigma_{id}$  vs. initial deformations  $\epsilon_0$  for HDPE at (■) 24°C, (▲) 50°C, and (●) 69°C.

resulting (straight) line with the stress axis is a measure of the internal stress. For natural reasons, the method can only be applied to the power-law portion of the relaxation curves.

Considering the  $\sigma_i$  value calculated according to Li, it follows from eq. (4) that it must be equal to  $\sigma_{ir} + \sigma_{id}$ . An application of Li's method to HDPE and LDPE is shown in Figure 4. The intercept with the  $\sigma$ -axis gives  $\sigma_i$  values

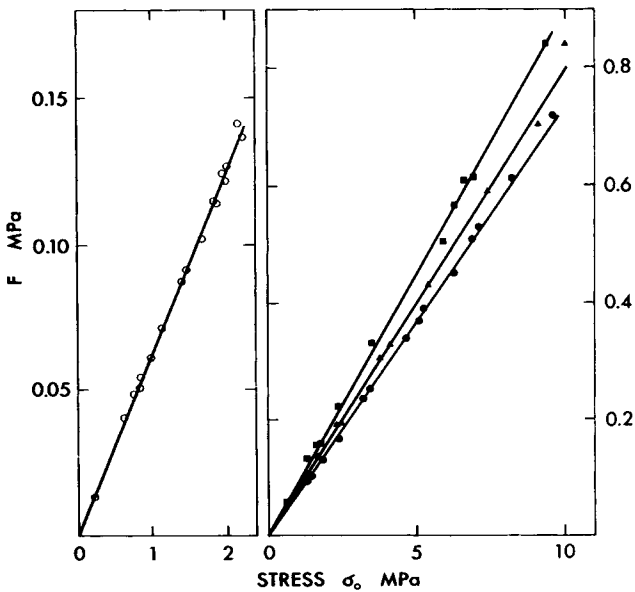


Fig. 7. Maximum slope  $F$  vs. initial stress  $\sigma_0$  for (○) LDPE at 24°C (left) and for HDPE at (■) 24°C, (▲) 50°C, and (●) 69°C (right).

TABLE I  
Mean Values of Exponent  $n$  Determined from the Slope of  $\log \sigma^*$  vs.  $\log t$

Material	Temperature, °C	$n$
HDPE	24	6-7
	50	6
	69	4
LDPE	24	6

of 0.21 and 1.4 MPa for LDPE and HDPE, respectively, to be compared with  $\sigma_0$  values of 1.07 and 13.9 MPa.

The results of Figure 5 show the approximate linear increase of  $\sigma_i$  with the initial stress  $\sigma_0$  for HDPE at varying temperature, indicating that  $\sigma_{ir}$  is zero. The constant of proportionality,  $c$ , in the relation

$$\sigma_{id} = c \sigma_0 \quad (8)$$

increases with temperature.

With LDPE, a somewhat different result was obtained, as the  $\sigma_{id}(\sigma_0)$  relationship was not linear. This is probably partly due to difficulties in applying Li's method at low stresses for LDPE.

The way in which the induced stress  $\sigma_{id}$  depends on stress and temperature (Fig. 5) suggests the possibility of  $\sigma_{id}$  being determined by the deformation only, irrespective of the temperature used. Figure 6, relating to HDPE, shows that this is approximately true.

We now proceed to the second method for the determination of an internal stress parameter. This method<sup>12,17,18</sup> relates to the exponential flow region. The maximum (inflexion) slope of the  $\sigma(\log t)$  curves is plotted versus the initial stress  $\sigma_0$ . The intercept of the resulting, usually straight, line with the  $\sigma_0$  axis gives the  $\sigma_i$  value. Contrary to Li's method, our procedure requires a number of relaxation curves to be recorded so that a sufficient number of  $F(\sigma_0)$  points can be plotted. On the other hand, it is always applicable, even in cases where Li's method due to an insufficient curvature of the  $\sigma(\log t)$  curves cannot be used. It can be shown<sup>18</sup> that the  $\sigma_i$  stress parameter emerging here gives the deformation-independent part of the total  $\sigma_i$  level, i.e., the residual stress  $\sigma_{ir}$  frozen in during the preparation of the sample.

What has been said about  $\sigma_{id}$  pertains also to  $\sigma_\infty$  as illustrated in Figure 3, provided  $\sigma_{ir}$  can be ignored. For instance, the variation of  $\sigma_{id}$  reflects the way in which  $\sigma_\infty$  will change when the initial stress  $\sigma_0$  is varied.

Figure 7 shows the slope  $F$ , defined as  $(-d\sigma/d \ln t)_{\max}$ , plotted versus the initial stress  $\sigma_0$  for LDPE at room temperature, and for HDPE at three different temperatures. The results show that the samples used were practically free from  $\sigma_{ir}$  (annealed samples). Earlier measurements produced similar results.<sup>15</sup> The slope of the  $F(\sigma_0)$  lines diminishes with increasing temperature, which according to eq. (6), is in agreement with the fact that the constant  $c$  in the relation  $\sigma_{id} = c \sigma_0$  increases with temperature.

In general, the two methods for determining the internal stress from stress relaxation data thus produce different values. There are, on the other hand, practically important instances where they may be equal. For instance, cold-drawn samples of polyethylene contain internal stresses of such a magnitude



that the deformation induced  $\sigma_{id}$  contribution at comparatively low deformations may be neglected. In such a case, both methods lead to practically the same result, that is, they both give the  $\sigma_{ir}$  value.<sup>12</sup> This further implies that the equilibrium stress  $\sigma_\infty$  remains practically independent of the initial stress  $\sigma_0$ .

With regard to the influence of internal stress on the kinetics of the relaxation process, the  $\sigma_i$  value entering the effective stress is the total internal stress  $\sigma_{id} + \sigma_{ir} = \sigma_i$ , this stress being equal to the equilibrium stress  $\sigma_\infty$ . In an extensive study of the relaxation behavior of polymers and metals, it was shown that the maximum slope of the  $\sigma(\log t)$  curves was proportional to the total dissipated stress, that is,  $\sigma_0 - \sigma_\infty$ , the constant of proportionality being independent of the structure of the sample.<sup>15</sup> The relation obtained was

$$F/(\sigma_0 - \sigma_\infty) = 0.1 \pm 0.01 \quad (9)$$

In the present investigation, the identities of the total  $\sigma_i$  value ( $\sigma_{id} + \sigma_{ir}$ ) and the equilibrium stress  $\sigma_\infty$  were demonstrated by considering the ratio

$$F/(\sigma_0 - \sigma_i) = k \quad (10)$$

where  $\sigma_i$  has been determined using the method of Li. The value of  $k$  obtained from these experiments was  $k = 0.10$  for HDPE, independent of the temperature used. For LDPE at 24°C, the value of  $k$  was 0.09. This agrees well with earlier findings.<sup>15</sup>

### The Stress Exponent $n$ in the Power Law

An important parameter describing the flow in the power-law region is the stress exponent  $n$ . The value of  $n$  can be determined either from the slope of plots of  $(-d\sigma/d \log t)$  versus  $\sigma$  or from the slope of the  $\log \sigma^*(\log t)$  curves.<sup>12</sup> Table I summarizes some typical  $n$  values. It may be noted that with regard to  $n$ , there is no differences between LDPE and HDPE at room temperature. A decrease in the value on  $n$  may be noted at higher temperatures. A similar trend has been reported for several metals.<sup>1</sup>

### The Activation Volume

Figure 8 (left) shows the variation of  $v$  with  $\sigma_0^*$  for LDPE and HDPE at room temperature, calculated from the exponential-law region, eq. (6), and its variation with the actual effective stress  $\sigma^*$  as determined from the power-law region, eq. (5). The value of  $v$  increases with temperature in accordance with eqs. (5) and (6). In the double-logarithmic plots used, the  $v(\sigma^*)$  line corresponding to the power-law region is shifted to the left when compared to the  $v(\sigma_0^*)$  line. The magnitude of this shift is given by  $n/10$ , eq. (7). Using the  $n$  values obtained, cf. Table I, makes it possible to transform the  $v(\sigma^*)$  and  $v(\sigma_0^*)$  data into each other. This has been done in Figure 8 (right). The stress dependence of  $v$  has been discussed in detail elsewhere.<sup>2,7</sup>

When discussing the stress dependence of  $v$ , it should be remembered that the inflexion slope  $F = (-d\sigma/d \ln t)_{\max}$  treated in the preceding sections is equal to  $kT/v$ . It, therefore, follows from eq. (10) and from the value of the constants entering therein that eq. (6) is valid for the PE samples investi-

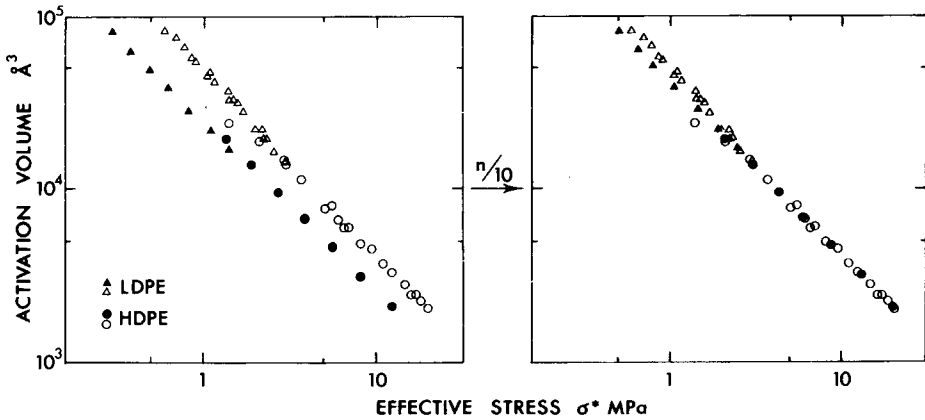


Fig. 8. Log-log representation of activation volume  $v$  determined from exponential-law region (unfilled markings) and power-law region (filled markings) vs. effective stress  $\sigma^*$  before (left) and after (right) shifting.

gated. Another important feature of the  $v(\sigma^*)$  data as presented in Figure 8 is that they can be transformed into each other irrespective of whether they have been determined from the exponential or the power-law region of the relaxation process.

## DISCUSSION

The two features of the stress relaxation process studied in this paper, that is, the internal stresses and the activation volume, are closely related. It has been known for some time that eq. (6) is of a rather general type and, within rather broad limits, independent of the structure of the material under study.<sup>2</sup> However, when the stress entering this relation is corrected for internal stresses, the scatter between different materials is almost entirely eliminated and one obtains  $v\sigma_0^* = 10kT$  for the exponential part and  $v\sigma^* = nkT$  for the power-law part of the relaxation curve.

With regard to internal stresses, the possibility of distinguishing between permanent and induced  $\sigma_i$  components is, no doubt, of interest both for reasons of practical use and for theoretical conclusions. Rather naturally, this distinction holds primarily for the region of low stresses only; a substantial increase in stress, involving, for instance, pronounced orientation effects, may result in an interaction between the two component  $\sigma_{id}$  and  $\sigma_{ir}$ . The reason why the division has not been used earlier may be associated with the fact that measurements of this type have been performed almost exclusively on certain engineering metals where the permanent  $\sigma_{ir}$  component could be very large<sup>19</sup> and the  $\sigma_{id}$  part very small. For polymers, however, the situation is different in that  $\sigma_{id}$  and  $\sigma_{ir}$  may assume comparable values, or, as in the examples shown above,  $\sigma_{id}$  may widely exceed  $\sigma_{ir}$ . To some extent, certain soft metals, such as Cd, may behave similarly.<sup>4</sup>

Considering the role played by the stress as flow rate-determining factor, one may notice that the exponential dependence expressed in eq. (3) only applies to the stress variation during a single relaxation experiment. The effect caused by changing the initial stress is entirely different in that this vari-

ation results in a linear increase of the flow rate. This is clearly borne out by the data presented above and also supported by earlier results.<sup>15</sup> The theory of stress-aided thermal activation cannot resolve this paradox without recourse to relations as eq. (6) prescribing an inverse-type relation between stress and activation volume.

The authors are indebted to the Swedish Board for Technical Development and to the Swedish Polymer Research Foundation for financial support.

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Received October 14, 1975

Revised December 4, 1975