PHYSICAL AGING OF POLYMERS

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Abstract — The general area of physical aging of polymers is reviewed. Various phenomenological aspects are introduced and discussed in terms of bulk structural changes evidenced by dilatometric and calorimetric studies, and are compared with the wide variety of information available from microstructural investigations involving spectroscopic and scattering techniques. Current models for describing the relaxation kinetics of the non-equilibrium glassy state are compared. Finally, the effects of physical aging on mechanical properties are reviewed, highlighting especially those areas which remain controversial.

Keywords — Physical aging, polymers, glasses, glass transition, enthalpy relaxation, volume relaxation, creep.

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**NOTATION**

<table>
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<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>$\alpha_f$</td>
<td>coefficient of thermal expansion of free volume</td>
</tr>
<tr>
<td>$\alpha_g$</td>
<td>coefficient of thermal expansion of glass of fixed structure</td>
</tr>
<tr>
<td>$\alpha_l$</td>
<td>coefficient of thermal expansion of equilibrium liquid</td>
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<tr>
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<td>exponent in KWW equation</td>
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<td>elementary values of $\delta$ in KAHR model</td>
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<td>$\tau^*$</td>
<td>&quot;coupled&quot; relaxation time</td>
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<td>$\tau_o$</td>
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<td>$\tau_3$</td>
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<td>$\tau_{\text{eff}}$</td>
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<td>$\tau_{ic}$</td>
<td>values of creep relaxation times in discrete distribution</td>
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<tr>
<td>$\tau_r$</td>
<td>rotational correlation time in ESR spectroscopy</td>
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<tr>
<td>$\phi$</td>
<td>stretched exponential function</td>
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<td>$\omega_C$</td>
<td>critical frequency in coupling model</td>
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<tr>
<td>$A$</td>
<td>constant</td>
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<tr>
<td>$a$</td>
<td>constant; or shift factor</td>
</tr>
<tr>
<td>$a_\delta$</td>
<td>shift factor for structure in KAHR model</td>
</tr>
<tr>
<td>$a_T$</td>
<td>shift factor for temperature in KAHR model</td>
</tr>
<tr>
<td>$b$</td>
<td>constant; or shift factor for $\Delta J$, relaxation strength</td>
</tr>
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</table>
C  constant; or denotes molecular chain centre
C_{pg}  specific heat capacity of glass of fixed structure
C_{pL}  specific heat capacity of equilibrium liquid
\Delta C_p  difference in specific heat capacities, C_{pL} - C_{pg}
c  shift factor for J_U, unrelaxed compliance
DMA  dynamic mechanical analysis
DMTA  dynamic mechanical thermal analysis
DSC  differential scanning calorimetry
E  denotes molecular chain end
E'  real part of complex modulus, storage modulus
E''  imaginary part of complex modulus, loss modulus
F  denotes free probe
f  fractional free volume; or frequency
f_g  fractional free volume at glass transition temperature T_g
g_i  strengths of individual elements in KAHR model
H  enthalpy
H_o  enthalpy at start of relaxation
H_t  enthalpy at time t during relaxation
H_\infty  enthalpy in equilibrium
HDPE  high density polyethylene
\Delta h^*  apparent activation energy
I  intensity of fluorescence spectroscopy
I(Q)  intensity of scattered Xrays in SAXS
I(0)  value of I(Q) when Q is extrapolated to zero
I_\infty  equilibrium intensity in fluorescence spectroscopy
I_3  relative intensity of orthopositronium in PALS
J  creep compliance
J_\alpha  compliance of \alpha-relaxation region
J_\beta  compliance of \beta-relaxation region
J_R  relaxed compliance
J_U  unrelaxed compliance
\Delta J  relaxation strength, J_R - J_U
KAHR  Kovacs–Aklonis–Hutchinson–Ramos (see ref. 38)
KWW  Kohlrausch–Williams–Watts (see refs 120 and 121)
k  Boltzmann’s constant
l  length
N  number of particles in SAXS
\bar{N}  average value of N
n  coupling parameter
o-PS  ortho-positronium
PALS  positron annihilation lifetime spectroscopy
PBT  polybutylene terephthalate
PC  polycarbonate
PMMA  polymethyl methacrylate
1. INTRODUCTION

The term "physical aging", as applied to polymers, encompasses a very wide range of behaviours, all of which are linked by the same phenomenon. This phenomenon is the observed change in a property of the polymer as a function of storage time, at constant temperature, at zero stress, and under no influence from any other external conditions. The multitude of properties used for observation has been the source of this wide range of behaviours, and includes both macrostructural, or bulk, properties...
such as specific volume, enthalpy, mechanical and dielectric response, as well as microstructural or molecular scale properties which may be probed by, for example, spectroscopic and scattering techniques. All of these properties have been reported to exhibit, under appropriate conditions, a behaviour which may be classified as aging. In addition, the prefix "physical" is often included in order to distinguish this phenomenon from those of chemical or biological aging. In the latter cases, changes in properties of the material are accompanied by irreversible changes in its structure, involving permanent chemical modification and rupture of primary atomic bonds, for example. In contrast, physical aging involves only reversible changes in properties, with no permanent modification of the structure, either chemical or physical, of the material. This distinction is important, and is fundamental to an understanding of the phenomenon.

The most common situation in which physical aging is observed is when an amorphous polymer is cooled from above to below its glass transition temperature $T_g$; the aging is then manifest as, for example, a reduction in the specific volume or enthalpy, and an apparent shift of the creep response to longer times. It should be stressed here that aging is not confined to amorphous polymers, nor is it initiated only by temperature changes, as will be discussed further below. Nevertheless, these observations in amorphous polymers provide an important clue to the origin of physical aging and its reversibility. The clue lies in the recognition that, since the aging polymer is in effect isolated from its external environment in respect of any interactions, then the driving force for the changes in properties must arise as a result of the non-equilibrium state of the material, and the thermodynamic requirement for an approach towards equilibrium.

In this respect, it is well known that amorphous polymers below $T_g$ are in a non-equilibrium state which can be characterised by thermodynamic quantities such as volume or enthalpy, and that the isothermal time-dependence of these quantities is easily measured. Furthermore, it is also accepted that an equilibrium state is readily achieved at temperatures above $T_g$. It is but a small step, therefore, to associate the phenomenon of physical aging with the non-equilibrium state of the glassy polymer. Indeed, in general terms, this is almost universally accepted as an explanation for aging behaviour in polymers. However, there still remains a number of unanswered questions relating in particular to: (i) the interaction between the fundamental thermodynamic quantities such as volume, enthalpy and entropy on the one hand and the mechanical properties such as creep and stress relaxation on the other hand; and (ii) the details of the molecular reorganisations which take place in order to accommodate the approach of these thermodynamic quantities towards an equilibrium state on aging.

The former question is clearly one of some technological and engineering significance. Thermoplastics, for example, are commonly melt processed, by techniques such as injection and blow moulding, extrusion, and film blowing. These processing techniques all involve a quench of the polymer from a high (melt) temperature to a low (typically ambient) temperature, and this is just the thermal history appropriate to the initiation of aging. Products processed in this way will therefore be anticipated to age at their service temperature, involving a time-dependent change in such properties as dimensions, density, modulus, compliance, refractive index and dielectric constant. A
proper engineering design should take into account physical aging effects, particularly if long service lifetimes are involved.

Neither is the latter question, concerning the details of molecular reorganisation during aging, of only fundamental scientific importance. It too can have an impact on possible technological advances in materials science and engineering. For example, following on from an understanding of the details of the structural changes that take place in the non-equilibrium glassy state, it may be possible to control this structure advantageously by a suitable combination of pressure, temperature, and stress histories, all of which are known to influence the non-equilibrium state.

This review does not provide the answers to these questions, but is written in such a way at least as to address them. First, the thermodynamic state of the glass is considered, in the way that it is characterised by volumetric and enthalpic measurements, and the general phenomenology of such structural relaxation is reviewed. In the light of these macroscopic or bulk properties, we then go on to consider the information available from spectroscopic and scattering techniques concerning the molecular scale rearrangements, and how this relates to structural relaxation. This is followed by a brief review of some theoretical models used to describe the volume and enthalpy changes that occur on aging, and a critical assessment of the extent to which they either represent the observed experimental data or reflect a physically realistic approach. Finally, the impact of physical aging on some mechanical properties is examined in detail, and is discussed in particular with reference to the extent to which the changes in mechanical properties on aging may be interpreted quantitatively in the light of the structural changes characterised by volume and enthalpy relaxation.

2. THE THERMODYNAMIC STATE OF THE GLASS

2.1. Background

The non-equilibrium thermodynamic state of a glass was first recognised well over half a century ago by Simon. He proposed that, on cooling (at constant pressure) from the equilibrium liquid, a transformation to a glass occurs at a temperature $T_g$ when the molecular rearrangements, needed for the material to accommodate to the changing temperature, slow down to such an extent that they require a time-scale longer than that available by virtue of the imposed cooling rate. In effect, a structure, which may be characterised by $T_g$, is "frozen in", and will be retained as long as the same cooling rate continues.

If the cooling is arrested at a temperature below $T_g$, then the glass will have excess thermodynamic quantities (volume, enthalpy, entropy) and there will be a driving force to reduce these towards equilibrium. Thus, at constant temperature, as time is allowed for the previously frozen-in molecular motions to be released, the phenomenon of physical aging will be manifest as a reduction in, most commonly, volume and...

†Strictly speaking, we should refer here to "retardation" rather than "relaxation", and in subsequent instances to volume retardation and enthalpy retardation. Such terminological distinction has, however, almost entirely disappeared from the literature nowadays. In keeping with common practice, therefore, we have adopted throughout the term "relaxation".
enthalpy. This reduction in excess values of volume and enthalpy will continue until a new equilibrium is established at the aging temperature. Unfortunately, the time-scales for equilibration become very long rather rapidly as the aging temperature is reduced, so that it is not usually possible to achieve equilibrium more than about 15°C below \( T_g \). There are two important practical implications of this: first, in experimental studies of physical aging, the equilibrium state (for example, volume or enthalpy) will not often be known, except by extrapolation from measured values at higher temperature; second, in engineering applications of polymers, physical aging will commonly occur throughout the service lifetime of the component. This basic thermodynamic description of the state of the glass has been universally accepted for very many years; indeed, the earliest thermodynamic treatments of Davies and Jones\(^3\),\(^4\) remain among the best today.

It is worth pointing out that the liquid to glass transformation can equally well occur at constant temperature on increasing the pressure. In this case, a glass transition pressure \( P_g \) would be defined by the freezing in of molecular motions, and the excess values of volume and enthalpy would be relaxed isobarically if a constant pressure greater than \( P_g \) were maintained. However, because of the increased experimental difficulty, such pressure studies of the glass transition have been undertaken only rarely; notable examples are the work of Hellwegge \textit{et al.},\(^5\) Rehage and Goldbach,\(^6\)\(^-\)\(^8\) McKinney and Goldstein,\(^9\) and more recently of Tribone \textit{et al.}\(^10\).

In the sections that follow immediately, therefore, we examine the volume and enthalpy relaxation behaviour at atmospheric pressure.

2.2. \textit{Dilatometry and Volume Relaxation}

Tool was one of the pioneers of dilatometry in glasses in the 1930's and 1940's. Unusually, his experiments on inorganic (silicate) glasses\(^11\)\(^-\)\(^13\) involved length rather than volume dilatometry, and the precision of his data is remarkable. From numerous studies involving various temperature and thermal histories, Tool established that isothermal recovery, following a temperature jump from an initial equilibrium state, could not be described by a kinetic equation in which the relaxation time \( \tau \) depended only upon the temperature \( T \). He proposed that \( \tau \) depended in addition upon the instantaneous state or structure of the glass during the relaxation, and he characterised this structure by means of the fictive temperature \( T_f \).

The fictive temperature can be defined by reference to the schematic length–temperature plot in Fig. 1. On cooling from equilibrium, the length will depart from the equilibrium line at \( T_g \) (which depends upon the cooling rate). Aging (or annealing) isothermally at a temperature \( T_a \) will allow the length to reduce from its original value \( \ell_o \) and approach equilibrium \( \ell_\infty \) at that temperature. After some aging time, the length will be \( \ell_t \). The fictive temperature, \( T_f \), of the glass in this aged state at time \( t \) is defined as the temperature at which the length would be equal to the equilibrium length (at \( T_f \)) if the specimen were instantaneously removed to that temperature. Thus the fictive temperature at the start of aging is equal to \( T_g \), and in equilibrium is equal to the aging temperature \( T_a \), during aging, it decreases from \( T_g \) to \( T_a \) in a manner that characterises the kinetics of the relaxation.
This dependence of $\tau$ on both $T$ and $T_f$ reflects what is called the non-linearity of the relaxation. The non-linear aspect of the relaxation is clearly seen in isothermal volume relaxation, which is the usual dilatometric technique employed, and the best examples are afforded by the work of Kovacs, summarised in his classical phenomenological study and review of the glass transition in amorphous polymers.\textsuperscript{14} Unfortunately, this article was written in French, so that although it is much quoted one suspects that it is seldom read; it shows clearly all of the essential features of structural (volume and enthalpy) relaxation, some of which seem often to be ignored, particularly by those who study only enthalpy relaxation. One of these features is non-linearity, which implies that the kinetics of isothermal recovery do not scale linearly with the magnitude of the departure. The most spectacular illustration of this is seen from a comparison of the recovery behaviour from initial departures which are equal but of opposite sign; under these circumstances a clear asymmetry is apparent.

Besides non-linearity, the other essential feature of structural relaxation is the presence of a distribution of relaxation times. Again, the clearest evidence of this comes from the work of Kovacs\textsuperscript{14} in the form of the so-called "memory effects". Suppose you take a glass which has been annealed for some time below $T_g$, reheat it rapidly to its fictive temperature, and then maintain the temperature constant. Because the sample is at its fictive temperature, the sample volume will, initially, be equal to the volume in equilibrium at that temperature. However, from this initial state, the sample volume is seen to depart from what is only an apparent equilibrium before returning finally to a true equilibrium. The explanation for this behaviour, in which the sample seems to have a memory of its previous thermal history, lies in the distribution of relaxation times; a single relaxation time theory is inadequate to describe such effects.

Another manifestation of this distribution can be seen when a glass is heated at a constant rate through the transition region. Under some circumstances, double peaks (rather than a single peak) in the thermal expansion coefficient are observed.\textsuperscript{15} More commonly, though, these double peaks are seen in differential scanning calorimetry (DSC), and are further discussed below.

Fig. 1. Schematic illustration of the variation of length with temperature in the glass transition interval: (i) on cooling; (ii) on annealing isothermally at temperature $T_a$; (iii) to illustrate the definition of fictive temperature $T_f$. Note that the same schematic diagram could also be used to illustrate the variation in volume $V$ or enthalpy $H$. 
The pioneering work of Tool and Kovacs effectively established the phenomenology of volume relaxation, in particular the existence of a distribution of relaxation times, and the non-linearity of the response. Since then, the rather few studies of volume relaxation have confirmed this phenomenology and have been aimed at a quantitative evaluation of the kinetics of volume relaxation in different polymer systems. In nearly all such studies, it is only isothermal volume (or length) contraction which has been monitored following a “down” temperature jump, though other thermal histories have occasionally been employed, including “up” temperature jumps leading to volume expansion, rate cooling, and rate heating experiments.

Isothermal volume contraction, however, whilst widely used is relatively uninformative about the overall relaxation kinetics. For example, consider the contraction isotherms shown in Fig. 2 for atactic polystyrene (PS), where the relative departure from equilibrium, $\delta$, is defined as the excess specific volume normalised with respect to the equilibrium volume:

$$\delta = \frac{v - v_\infty}{v_\infty}$$

(1)

The relaxation is much slower than exponential, as is always observed, and this could be explained either by non-linearity (relaxation time dependent upon $\delta$) or by a distribution of relaxation times, or by both: these contraction isotherms alone cannot distinguish between them. The simple quench, or “down” temperature jump, does not therefore provide, in itself, a very critical examination of the aging process.
Care also needs to be exercised in the interpretation of the volume relaxation rate, \( \beta \), defined in terms of the inflectional slope of these isotherms,\(^{14}\)

\[
\beta = -\frac{d\delta}{d\log(t - t_i)} \approx -\frac{1}{v} \frac{dv}{d\log(t - t_i)}
\]  

This quite widely used parameter\(^{14,16,19,23,26}\) is often used to compare the recovery kinetics at temperatures well below \( T_g \). The problem lies in ensuring that the inflection of the contraction isotherm is indeed reached, particularly at low temperatures. Although these isotherms are observed, as in Fig. 2, to display a rather wide time interval over which a linear relationship pertains, there is clearly a delay before the truly inflectional slope is reached. This effect is well illustrated by reference to the half-filled circles in Fig. 2 (see legend) which represent a measure of this delay. With reducing temperature, this “delay time” increases; the data here and those of Kovacs\(^{14}\) on polyvinyl acetate (PVAc) suggest a shift of 1 decade in 35°C, approximately. Furthermore, the inflectional tangent is not reached until over half a decade beyond this delay time. Thus in PS at 20°C (i.e. 70°C below the lowest temperature in Fig. 2), one might anticipate that the true inflectional slope is not reached until an aging time of at least 6 h. As has been suggested by Greiner and Schwarzl,\(^{19}\) this could be the origin of differences in the values of \( \beta \) obtained by various authors if insufficiently long aging times are used.

2.3. Calorimetry and Enthalpy Relaxation

Probably the main reason for the limited number of dilatometric studies of the glass transition in polymers is the lack of suitable commercial equipment. In contrast, calorimetric studies are extremely numerous, particularly by differential scanning calorimetry (DSC), though adiabatic calorimetry has been used for more “exotic” glassy systems.\(^{28–30}\) The technique of DSC is used to determine the enthalpy of a glassy polymer in order to characterise its structural state, and this is analogous to the volume determined by dilatometry. However, it is essential to recognise the fundamental differences between the two techniques.

In DSC, it is the specific heat which is measured as a function of temperature on heating at constant rate. Enthalpy changes on aging below \( T_g \) are found by integration of appropriate DSC curves, as illustrated schematically in Fig. 3. The initial enthalpic state at A is achieved reproducibly by cooling at a controlled rate from equilibrium at a temperature \( T_o > T_g \). On aging at temperature \( T_a \), the enthalpy reduces, and after time \( t \) it has the value \( H_t \) at B. The difference in enthalpy between A and B, i.e. the enthalpy lost on aging, is found from the DSC traces of Fig. 3(b) as the difference in the areas under these curves between the aging temperature \( T_a \) and the temperature \( T_o \) at which equilibrium has been attained in both cases. Superposability of the two curves in their asymptotic glassy and liquid regimes is essential for accurate results, and the usual procedure is to re-scan the same sample for zero aging time (curve A) immediately after the scan for the aged state (curve B). This eliminates errors due to sample-to-sample variation, instrumental baseline and calibration drift, and differences in location of the sample within the DSC cell.
Fig. 3. Schematic illustration of (a) enthalpy vs temperature plot, and (b) specific heat vs temperature curves. State A is reached by cooling at constant rate from equilibrium at $T_0$; state B is reached after subsequently aging at $T_a$ for time $t$. The lower figure shows typical DSC traces on heating from each of these states. The dashed line in the upper figure represents the equilibrium enthalpy-temperature curve, and $H_\infty$ is the value of the enthalpy in equilibrium at $T_a$.

This approach has been adopted since the early work of Petrie,\textsuperscript{31} though it is in addition common practice to quench the sample from B to a lower temperature and to start the DSC scan from there, in order to overcome some problems of thermal inertia; this procedure is valid as no enthalpy changes will occur during the short period of time that the sample spends below $T_a$.

Given sufficient aging time at $T_a$, the enthalpy relaxation will proceed to equilibrium, where the enthalpy is $H_\infty$. The analogous quantity to $\delta$, the relative departure from equilibrium in dilatometric experiments (see eq. 1), is the excess enthalpy defined as:

$$\delta_H = H_t - H_\infty$$

and the evolution of $\delta_H$ with time will give the enthalpy relaxation data analogous to volume contraction isotherms.

One of the major problems here is the evaluation of $H_\infty$, as has recently been discussed in some detail.\textsuperscript{32} Unlike in volume relaxation, where equilibrium is clearly seen (refer to Fig. 2) when there is no further change in volume with log time, in enthalpy relaxation new samples with increasing log (aging time) must be scanned
and this procedure repeated until no further change in $H_0 - H$ is observed. This is not, in itself, a problem, but it has a number of attendant difficulties.

(i) Volumetric equilibrium in PS (refer to Fig. 2) is achieved within the "reasonable" time-scale of 100 h for aging temperatures only down to about 10°C below $T_g$ (taking $T_g = 105°C$). This is consistent with the WLF prediction for the dependence of $T_g$ on cooling rate: a change of approximately 3°C per decade of time. Enthalpy relaxation time-scales are usually considered to be longer than those for volume relaxation (e.g. see refs 21 and 31), and enthalpic equilibrium is therefore likely to be achieved experimentally only in a very limited temperature interval below $T_g$. This is further compounded by the fact that experimental error is generally larger in the measurement of $\delta_H$ than $\delta$, thus creating greater difficulties in the identification of enthalpic equilibrium.

(ii) At lower temperatures, equilibrium (either volumetric or enthalpic) will never be achieved within an accessible time. For dilatometry, linear extrapolation over a reasonable temperature interval from equilibrium values at higher temperatures will give acceptable values for $v_\infty$, since the thermal expansion coefficient is approximately constant. Such extrapolation is not recommended for calorimetry, since the specific heat is not constant with temperature. Alternative procedures, such as treating $H_\infty$ as an adjustable parameter in an empirical equation for enthalpy relaxation, are extremely dubious, particularly when the experimental time span for relaxation data is short. Unfortunately, this procedure is all too often used, and it is best to ignore such results, along with those which purport to identify an equilibrium state from enthalpy relaxation data plotted against a linear timescale.

In respect of isothermal relaxation, therefore, calorimetry compares unfavourably with dilatometry. In addition, since enthalpy is not the measured variable in DSC, the method of determination of both the glass transition temperature $T_g$ and the fictive temperature $T_f$ is not immediately obvious, as it is in dilatometry (refer to Fig. 1). In fact, there is considerable confusion in the literature regarding these determinations, compounded by the fact that commercial DSC software utilises $T_g$ definitions, such as "onset $T_g$" and "mid-point $T_g$", which are at best only approximations to the conventional $T_g$. The problem is easily identified. $T_g$ is an operational definition of a temperature at which the melt transforms to a glass on cooling, whereas the DSC utilises a heating scan, on which the whole thermal history of the glass (i.e. prior cooling and annealing at $T_a$) will have an influence. In fact, it is meaningless to refer to a "glass transition temperature" of a glass in state B in Fig. 3(a); the fictive temperature is the relevant parameter, and for zero annealing time (state A in Fig. 3(a)) the fictive temperature and the glass transition temperature are identical. The determination of $T_f$ for a glassy sample requires the integration of DSC heating scans, and appropriate procedures were originally proposed by Richardson and Savill and by Moynihan et al. Happily, such analysis is now included in Perkin-Elmer DSC software.

Furthermore, the type of isothermal enthalpy relaxation illustrated in Fig. 3(a) is, like its volumetric counterpart discussed above, not very informative about the
underlying kinetics. Such studies are therefore of rather limited value. Much more informative is the examination of the DSC heating scan, schematically illustrated in Fig. 3(b), as a function of the experimental variables defining the "three step" thermal cycle: cooling rate, annealing time and heating rate.\(^3\) Of these, the annealing time (or \(\delta_H\), the difference in the values of \(\delta_H\) at the start and end of the annealing period) is the most widely exploited. The effect of increasing the annealing time, whilst maintaining the other variables constant, is illustrated in Fig. 4 for polymethyl methacrylate (PMMA). This result is typical; an increase in the magnitude of the endothermic peak and a shift of the peak to higher temperature as the annealing time (and \(\delta_H\)) increases. It is also typical to find a linear dependence of both \(\delta_H\) and the peak temperature, \(T_p\), on log (annealing time) over a wide range of annealing times. The former is, of course, just the isothermal enthalpy relaxation, and linear dependence corresponds to the linear reduction of \(\delta\), in volume relaxation, with log (annealing time).

The dependence of \(T_p\) on log (annealing time), on the other hand, has been shown to be determined essentially by the degree of non-linearity of the relaxation behaviour.\(^3\) More generally, the whole of the heating scan is rather sensitive both to the experimental variables and to the material parameters describing the kinetics of the relaxation, and has been the subject of considerable research in polymer and inorganic glasses,\(\dagger\) as well as on other glassy systems. The objective of these studies is to evaluate the material parameters on the basis of some theoretical models discussed further below.

\(\dagger\)The literature in this area is voluminous. A very recent review\(^4\) gives an excellent and comprehensive survey. For some typical examples, the reader is referred to refs 42–47.
Table 1. Values of the volume relaxation rate, $\tilde{\beta}$ (eq. 2), for selected polymer glasses. These rates are evaluated approximately 15°C below $T_g$.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\tilde{\beta} \times 10^4$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbonate</td>
<td>8.5</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>8.3</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>&gt;8.0</td>
<td>23</td>
</tr>
<tr>
<td>Polyvinylacetate</td>
<td>7.9</td>
<td>14</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>8.0</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>7.7</td>
<td>16, 23</td>
</tr>
<tr>
<td></td>
<td>8.1 ($M_w = 210,000$)</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>6.8 ($M_w = 300,000$)</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>this work</td>
</tr>
<tr>
<td>Polyethyleneterephthalate</td>
<td>5.4</td>
<td>23</td>
</tr>
<tr>
<td>Polymethylmethacrylate</td>
<td>4.6</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>3.7</td>
<td>23</td>
</tr>
<tr>
<td>Polyvinylchloride</td>
<td>3.5</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>&gt;2.6, 3.5</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>3.1</td>
<td>24</td>
</tr>
<tr>
<td>Epoxy resin</td>
<td>1.4</td>
<td>18</td>
</tr>
</tbody>
</table>

2.4. Comparison of Dilatometric and Calorimetric Studies

In the simplest situation, following a quench from above to below $T_g$ both the volume and the enthalpy reduce with log (aging time) in a similar, but not identical, way.

The volume relaxation rate, $\tilde{\beta}$ (eq. 2), passes through a maximum about 15°C below $T_g$, and shows quite large variations between different polymers, as can be seen in Table 1 above, where data for selected polymers are given. It is remarkable, for example, that PS, PVAc and polycarbonate (PC) display large rates, whereas the rate is much smaller for polyvinylchloride (PVC) and PMMA, and considerably so for epoxy resin.

The equivalent enthalpy relaxation rates defined as:

$$\tilde{\beta}_H = -\frac{d\delta_H}{d\log t}$$

and evaluated at a temperature 15–20°C below $T_g$ can be seen in Table 2. There does not appear to be any simple correlation with the volume relaxation rates shown in Table 1. Thus, although PMMA and PVC again display low relaxation rates, and PVAc and PS again give high rates, the enthalpy relaxation rate for PC seems unusually low, while that for epoxy resin is remarkably high.

Furthermore, consideration of the relative timescales for volumetric and enthalpic equilibration also raises some unanswered questions. It is surprising that this should remain so controversial an issue at this time. Nearly 25 years ago, Petrie\textsuperscript{31} noted that the times required for relaxation of enthalpy are considerably longer than those for volume relaxation. Her data in Fig. 6 of ref. 31 support this: enthalpic equilibrium in
Table 2. Values of the enthalpy relaxation rate for the polymer glasses listed in Table 1, evaluated approximately 15°C below $T_g$

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$\beta_H/J_g^{-1}$ per decade</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polycarbonate†</td>
<td>0.62</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>0.56</td>
<td>50</td>
</tr>
<tr>
<td>Polyvinylacetate</td>
<td>1.12</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>0.88</td>
<td>52, 53</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.78</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>31</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.77</td>
<td>55</td>
</tr>
<tr>
<td>Polyethyleneterephthalate</td>
<td>1.13</td>
<td>56</td>
</tr>
<tr>
<td>Polymethylmethacrylate†</td>
<td>0.48</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>59</td>
</tr>
<tr>
<td>Polyvinylchloride†</td>
<td>0.39</td>
<td>21</td>
</tr>
<tr>
<td>Polymethylmethacrylate†</td>
<td>0.34</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>61</td>
</tr>
<tr>
<td>Epoxy resin†</td>
<td>1.04</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>0.81</td>
<td>63</td>
</tr>
</tbody>
</table>

†Values of $\beta_H$ for PC, PMMA and PVC can also be found from the data of Ott, but they are very much larger than those given above. Similarly, Liu et al. and Plazek and Frund quote exceptionally large values for PC and epoxy resin, respectively. The reasons for these discrepancies are not known.

PS at a temperature about 8°C below $T_g$ requires more than 100 h of aging time, whereas volumetric equilibrium at an equivalent temperature is achieved in only about 10 h. This author has seen no reliable evidence to controvert this observation; however, it must be said also that no definitive study has yet been made to compare, for the same polymer, at the same temperatures with respect to their $T_g$'s, the volumetric and enthalpic equilibration times.

It is important to resolve this problem if the fundamental origins of physical aging are to be understood. If enthalpy relaxation continues in volumetric equilibrium, then there are some molecular motions which contribute to enthalpy relaxation, but involve no change in volume. This would indeed be suggested by the different rankings of volumetric and enthalpic relaxation rates in Tables 1 and 2. The question arises then whether or not these molecular motions can contribute also to, for example, the changes in mechanical properties which occur on aging. Some consideration is given in the next section to the kind of information about these molecular motions that can be obtained from experimental techniques which probe the microscopic rather than macroscopic structure of the glass.

3. MICROSTRUCTURAL ASPECTS

3.1. Introduction

One of the remarkable features of structural (i.e. volume or enthalpy) relaxation is its universality; the same phenomenology is seen in a wide variety of glassy systems, including inorganic and, to a certain extent, metallic glasses, low molecular weight...
compounds, and amorphous, liquid-crystalline and cross-linked polymers. This suggests that the glass transformation process and the associated structural changes that occur in the non-equilibrium glassy state are rather general, and are not associated with specific details of chemical structure.

This aspect of aging must be borne in mind when considering a physical or molecular interpretation of the observed phenomena. It is common, therefore, to make reference to quantities such as "free volume" and "configurational entropy", which have a physical meaning to be discussed further below, and experimental techniques for microstructural analysis in physical aging are usually interpreted in terms of the former. These techniques can broadly be separated into spectroscopic probe and scattering methods. The following is not intended to be an exhaustive survey of such methods; rather it is intended to convey the typical information that emerges from such studies, and what clues this provides as to the nature of the aging process.

3.2. Positron Annihilation Lifetime Spectroscopy

The technique of positron annihilation lifetime spectroscopy (PALS) has recently found increasing application to the physical aging of polymers, on account of its reputed ability to measure directly both free volume and the distribution of free volume. The positron (e+) is the antiparticle of an electron; when injected into a polymeric material it can either, as a free positron, annihilate directly with an electron, with a mean lifetime of less than 0.5 ns, or it can capture an electron to form a bound state, known as a positronium atom (Ps). Two states, with different lifetimes, are possible. For PALS, the more important is the ortho-positronium (o-Ps), an electron–positron state with parallel spins, which has a mean lifetime (τ3) of 142 ns in vacuo. In condensed matter, the lifetime of o–Ps is considerably reduced because it can pick off and annihilate with an electron with anti-parallel spin. The o–Ps is concentrated in free volume "holes" within the polymer, and it can be shown theoretically that the lifetime τ3 is proportional to the hole size. Furthermore, the relative intensity (I3) of the o–Ps component provides a measure of the number of holes, so that a more detailed analysis of both τ3 and I3 can give an estimate of the hole size distribution. The determination of τ3 and I3 as a function of aging in polymers therefore clearly offers some exciting possibilities. Since o–Ps has a radius of about 0.05 nm, it should be able to probe holes (assumed to be spherical) of this kind of size, and the upper limit on the radius of a hole may, in principle, be as large as 1.0 nm.

Strong support for the usefulness of PALS comes from the studies of Jean et al. on the effects of pressure in polypropylene and epoxy resins. For both polymers, an increase in pressure results in a reduction in hole size, as measured by τ3, as expected. In addition, though, the distribution of hole radii is found to narrow as the hole size decreases. These kinds of details would be interesting to examine in physical aging, but the experimental evidence to date is much less convincing, for two reasons.

First, whereas changes in τ3 with pressure are quite large (for example, from 2.3 to 0.7 ns as the pressure is increased from zero to 14.7 kbar in polypropylene, and from
1.6 to 0.5 ns for the same pressure range in epoxy), the changes in $\tau_3$ on aging are much less dramatic. For example, in PVAc aged at 20°C, about 12°C below $T_g$, $\tau_3$ decreases from 1.9 to only 1.8 ns, approximately, over an aging period of 100 h, even though there is a strong temperature dependence of $\tau_3$ which allows $T_g$ to be defined rather clearly. A similar effect, whereby $\tau_3$ is relatively unaffected by aging but displays a strong temperature dependence, is seen on aging PC at both 30 and 90°C, though these temperatures are both very low with respect to $T_g$, which is at approximately 140°C from these PALS data; only a small reduction in $\tau_3$ is also seen on aging PC at 120°C over 50 h. Despite the fact that these data are presented versus linear aging time rather than log (aging time), as would have been more appropriate, it nevertheless appears that the effect of aging on $\tau_3$ is different from that of temperature: on changing the temperature, the free volume holes change significantly in size, whereas on aging they reduce in size by only a very small amount, but must reduce appreciably in number in order to accommodate the reduction in volume.

The above-mentioned representation of aging time on a linear time scale is unfortunately not only rather prevalent, but is also very misleading. For example, the rather extensive studies by Hill et al. of physical aging and thermal history effects, particularly in PC, but also in other polymers, are critically marred by the erroneous conclusion, derived from $o$-Ps intensity $I_3$ versus linear time, that equilibrium is established in PC after only a few hundred hours at 50°C. On the contrary, to reach a fictive temperature of 50°C in PC, nearly 100°C below $T_g$, would require geological time scales.

This leads us to the second reason why the aging data in PALS are not entirely convincing. It is commonly observed that $I_3$ (i.e. the number of free volume holes) reduces on aging much more significantly than any changes in $\tau_3$, and this is used to explain how free volume can be lost on aging without any significant change in hole size. Some recent results though, suggest that this reduction may, at least in part, be due to radiation effects from the source, which seem to influence $I_3$, but not $\tau_3$. For example, Kluin et al. find for PC a reduction in $I_3$ on aging at 23°C even for an "as-received" (i.e well aged) sample, and conclude that the intensity reduces with positron exposure time. O'Connor et al. reach the same conclusion from experiments in which the PS sample is first analysed by PALS and then removed from the source for a long period of time (98h) before being re-analysed; even though the aging time is much longer in the second analysis, the decay in $I_3$ is observed to be identical to the first analysis. Li and Boyce achieve the same effect and results in both PC and PS by analysing successively the two sides of the same sample, only one side being exposed to radiation at any time. The inescapable conclusion is that the reduction in $I_3$ is an artefact of radiation exposure, which builds up an electric field in these insulating polymers and thus reduces the probability of positronium formation. The solution to this problem must be to remove the sample from the radiation source when PALS measurements are not being made.

A further disadvantage of the PALS technique is that it requires at least about 0.5 h to collect sufficient counts for a spectrum, whilst the recommended 10 M counts may require as long as a day. Even for 0.5 h, this would imply a minimum aging time of
the order of 5 h to ensure that the aging state did not change significantly during the PALS analysis, thus eliminating the possibility of examining what happens at short aging times. At present, therefore, the application of PALS to physical aging in polymers appears both limited and subject to some careful interpretation of the data.

### 3.3. Electron Spin Resonance Spectroscopy

The technique of electron spin resonance (esr) spectroscopy allows the structure of polymers to be interpreted from the detailed tumbling motion of nitroxide radicals as they rotationally diffuse in a way that is sensitive to their local environment. Specifically, spin probe techniques utilise stable radicals which are diffused into the polymer, whereas spin labels refer to radicals covalently bonded to the host polymer. This tumbling of the radical yields an esr absorption spectrum which can be characterised by a rotational correlation time $\tau_r$. In particular, two quite different spectra are seen for different ranges of $\tau_r$: the motionally narrowed region where $10^{-11} \text{s} < \tau_r < 10^{-8} \text{s}$ and the extrema separation is above 30 G and the slow motion region where $10^{-8} \text{s} < \tau_r < 10^{-6} \text{s}$ and the separation is much wider, about 70 G.

With increasing temperature, as $\tau_r$ decreases, there is a rather abrupt change from the slow motion to the motionally narrowed region, with the extrema separation becoming very sensitive to $\tau_r$, particularly at about 50 G. The temperature at which this occurs is thus referred to as $T_{50G}$. This temperature depends upon the size of the probe, with smaller probes such as TEMPO (2,2,6,6-tetramethyl-piperidine-1-oxyl) and TANOL (4-hydroxy-2,2,6,6-tetramethyl-piperidine 1-oxyl) having lower values of $T_{50G}$ than larger probes and spin labels.

The dependence of $T_{50G}$ upon aging time does not appear to be very strong, and is therefore not a sensitive measure of structural changes during aging. On the other hand, the details of the esr spectral shape can be rather revealing. In particular, the spectra for many amorphous polymers are of a composite nature, exhibiting both fast and slow motion components, even at temperatures well below the glass transition temperature. These have been shown to arise from a distribution of correlation times which can in turn be interpreted in terms of a distribution of free volume. In addition, the existence of the mobile components of the spectra at low temperatures is indicative of free volume regions, greater than the size of the probe, deep in the glassy state. Some calculations of the most probable size of free volume holes in PMMA at various temperatures have been given by Tsay and Gupta, and may be compared with values found from PALS, but the usefulness of esr spectroscopy in understanding physical aging really depends upon the development of a more quantitative analysis.

### 3.4. Fluorescence Spectroscopy

The use of fluorescent molecules as probes of molecular mobility was first demonstrated by Loutfy in the course of some studies on free radical polymerisation. He observed a sharp rise in fluorescence as the viscosity rose rapidly during the
polymerisation of PMMA indicative of a sensitivity to glassy state structure. The technique employs a suitable fluorescent molecule, such as julolidenemalononitrile (JMN), which on absorbing light is elevated to an excited state. There are two routes for this molecule to return to its ground state: a non-radiative mechanism involving various bond rotations in the probe, and a radiative mechanism involving photon emission and fluorescence. If the bond rotational motion within the probe is hindered by a lack of molecular mobility, then the former mechanism cannot provide a route back to the ground state, and the latter mechanism becomes dominant. Thus a reduction in molecular mobility will be evidenced by an increase in fluorescence intensity.

The number of studies of physical aging in polymers by fluorescence spectroscopy is rather limited, but the results are encouraging. Meyer et al.\textsuperscript{9} show not only that the fluorescence intensity in PVAc can define a $T_g$ on cooling which is very close to that determined calorimetrically, but also that the intensity increases significantly on aging below $T_g$ following a quench. Royal and Torkelson\textsuperscript{10} also studied PVAc but included more thermal treatments than a simple “down” temperature jump. By analogy with volume relaxation (eq. 1) they define a relative departure of the intensity $I$ from an equilibrium value $I_\infty$ as:

$$\delta_F = -\frac{I - I_\infty}{I_\infty}$$  \hspace{1cm} (5)$$

Remarkably, the time evolution of $\delta_F$ during aging following “down” and “up” temperature jumps, as well as more complex thermal histories leading to “memory effects”, parallels the bulk volume relaxation behaviour;\textsuperscript{14} even the $\tau_{\text{eff}}$ paradox\textsuperscript{14} is mirrored in these fluorescence spectroscopic data. This technique is probing mobility on a molecular scale, and these results are consistent with the existence of a distribution of free volumes corresponding to the distribution of relaxation times for bulk properties. Interestingly, the timescale for equilibration of the intensity is very similar to that required for enthalpy relaxation, at least at temperatures just below $T_g$. If enthalpy relaxation has a longer timescale than does volume relaxation, then the free volume interpretation above of the fluorescence data would be difficult to justify; this emphasises the importance of resolving the question of timescales for relaxation of different properties.

A later study by the same authors\textsuperscript{91} extended the range of polymers to include PS, PMMA, PC and poly(isobutyl methacrylate), but only for thermal histories involving “down” quenches. For all polymers, an approximately linear increase in normalised intensity with log (aging time) was observed, similar to volume and enthalpy relaxation, from which the slopes can be evaluated. These slopes, like $\bar{\beta}$ and $\bar{\beta}_H$ for volume and enthalpy, respectively (eqs 2 and 4), are seen to pass through a maximum as the temperature of aging is reduced below $T_g$. Care must be exercised in a comparison of their absolute magnitudes between different polymers, though, since the equivalent “fluorescence aging rate”, defined as:

$$\bar{\beta}_F = -\frac{d\delta_F}{d \log t} = \frac{1}{I_\infty} \frac{dI}{d \log t}$$  \hspace{1cm} (6)$$
involves the equilibrium intensity, \( I_\infty \), in addition to the slope of \( I \) versus log time. Indeed, if the slopes alone are compared, at approximately equivalent temperatures below \( T_g \), for PC, PS and PMMA from the data of Royal and Torkelson,\(^9\) then these polymers are arranged in the opposite order to that for volume relaxation (Table 1).

The fluorescence response is seen therefore, to be closely similar to bulk relaxation processes, and can be interpreted in terms of both free volume, which provides the molecular environments in which the probe molecule has a restricted degree of mobility dependent upon the aged state of the polymer, and of a distribution of such free volume sites.

### 3.5. Photochromic Probes and Labels

Free volume environments in glassy polymers can also be investigated by means of photochromic probes and labels. In the same way as for the nomenclature in esr spectroscopy, a probe is dispersed freely within the polymer matrix, whereas a label is bonded chemically to the polymer molecule. Both probes and labels are commonly used in this technique, which is based upon following the photochemically induced \( trans\-cis \) isomerisation of the chromophore. The absorption of light over a range of wavelengths induces in the chromophore a reversible change from the \( trans \) to the \( cis \)-isomer. These two species have different absorption spectra, and the changes can be observed by UV-vis spectroscopy. The photoisomerisation process is dependent upon there being sufficient molecular mobility for the chromophore, which is determined by its free volume environment. Thus the aging process can be monitored by changes in the absorption spectrum.

Lamarre and Sung\(^9\) were the first to demonstrate how physical aging in polymers could be monitored by photochromic labelling, using some amorphous, low-\( T_g \) polyurethanes. They showed that the kinetics of the isomerisation in dilute solution is very different from that in the glassy solid, where there is restricted mobility. In fact, they could characterise the kinetics in the solid in terms of two separate processes: a fast process with a rate constant similar to that in dilute solution, and a slow process with a rate constant about two orders of magnitude smaller. This is certainly, though, an oversimplification; more generally one would argue that these results imply a distribution of free volume sites, with the fastest rates occurring where the photochromic label exists in a region with free volume greater than a critical size.

This technique was further refined in a later study\(^9\) which utilised both a free probe (F) and also labels selectively attached to the molecular chain ends (E), side chain (S) and chain centres (C) in polystyrene. It was found that the free probe had the largest fraction of fast processes, or in other words, had in its vicinity the largest proportion of free volume sites; the labels followed in decreasing order E, S and C, with the chain centres having only a very small proportion of fast processes. On aging, it was primarily the E and S labels which were affected. For the free probe, even after aging (for rather short times, of the order of 1 day maximum, usually) their sites remained greater than the critical size, whereas for the C labels, their environment was already almost entirely of free volume sites less than the critical volume, and aging would not change this significantly.
The same idea concerning the existence of a critical free volume for photo-isomerisation in the glassy state has been investigated in an alternative way.\textsuperscript{94-97} By taking photochromic probes of various sizes, Torkelson \textit{et al.} were able to estimate the distribution of free volume in some glassy polymers, and to examine the effect of aging on this distribution, by comparison with the volumes required for the probes to isomerise, derived from van der Waal’s radii. For example, for PS they estimated that more than 90\% of the free volume exists in sites larger than 120–130Å,\textsuperscript{3} with no site being larger than 400 Å.\textsuperscript{3} More generally, the aging of PS, PMMA and PC are all characterised by a rapid reduction in the fraction of sites with large free volume. In fact, this reduction is incompatible with measurements of bulk volume relaxation, by approximately an order of magnitude, unless it is assumed that this free volume is redistributed to sites of smaller local free volume.

It is also interesting to note that some of the specific differences observed between the different polymers studied. For example, PMMA is found to have a larger size distribution of free volumes than does PS, which is consistent with a more “stretched” response for PMMA in both volume and enthalpy recovery (lower values of $\beta$ and $\beta_H$). Although it is difficult to reconcile some of the other observations with bulk properties, the technique of using photochromic probes and labels provides significant insight into the general structural changes occurring on physical aging, as well as into some of the details specific to some particular glassy polymers.

\textbf{3.6. Small Angle X Ray Scattering}

All of the techniques discussed above are spectroscopic probe or labelling methods. A quite different approach is to use scattering techniques, which may include neutron scattering, light scattering and, in this particular instance, small angle X ray scattering (SAXS). A common feature of all the spectroscopic techniques is the rationalisation of the observations in terms of a distribution of free volume; such a distribution may also be referred to as density fluctuations, which in a single component system are responsible for the scattering of electromagnetic waves, and hence are directly measurable experimentally by SAXS. This scattering technique therefore provides another way of looking at the structural changes which occur on aging.

From statistical mechanics, the following equation for thermal density fluctuations may be derived\textsuperscript{98} for polymer melts in terms of the number $N$ of particles (electrons or atoms) falling within a volume $V$ and fluctuating around their mean $\bar{N}$:

$$\frac{\delta N^2}{\bar{N}} = \frac{(N - \bar{N})^2}{\bar{N}} = \rho_N kT \kappa(T)$$

(7)

where $\rho_N$ is the particle density and $\kappa(T)$ is the isothermal compressibility.

The SAXS data can be presented either as density fluctuations, $\delta N^2 / \bar{N}$ as given by eq. 7, or as the intensity $I(Q)$ of the scattered X rays, $Q$ being the magnitude of the scattering vector ($= 4\pi \sin \theta / \lambda$); the intensity is often given as $I(0)$, the value when $Q$ is extrapolated to zero.

On cooling into the glassy state, eq. 7 no longer holds; density fluctuations are frozen-in at their value at the glass transition temperature.\textsuperscript{99} More generally, the
density fluctuations will depend upon the way in which the glassy state was reached, and will be a function of both the actual temperature and the fictive temperature:

$$\frac{\delta N^2}{\bar{N}} = \rho_N k T \kappa(T_f)$$

Thus SAXS experiments would be expected to measure the response to changes in fictive temperature on aging.

Wendorff and Fischer\textsuperscript{98} and Ruland \textit{et al.}\textsuperscript{100,101} were the first to demonstrate its applicability to the study of glassy polymers, and an early success of the technique was to demonstrate\textsuperscript{102,103} that there was no evidence to support the suggestion that “nodular” structures of locally ordered regions existed in polymer glasses, as had been proposed some time earlier by Yeh and Geillo\textsuperscript{4} on the basis of electron microscopic evidence.

When applied to physical aging of PC, PS and PMMA though, the SAXS results are rather surprising. On cooling at constant rate through the transition region, a change in slope of $I(0)$ or $\delta N^2 / \bar{N}$ as a function of temperature is observed at a temperature roughly corresponding to $T_g$, and on reheating a degree of hysteresis is seen. This is to be expected. What is surprising though, is that, on aging below $T_g$, there is very little change in the density fluctuations\textsuperscript{99,105,106} or else the changes occur in a very limited temperature interval around $T_g$\textsuperscript{107} even though the volume (and enthalpy) reduces significantly.

One explanation could be simply that the timescale for changes in density fluctuations is very much longer than that for volume relaxation\textsuperscript{99} but another, and rather interesting, possibility is that the free volume decreases, in line with the observed decrease in the macroscopic volume, but that the average size of a free volume hole increases during aging.\textsuperscript{105,106} This latter suggestion resembles the results from PALS which show a significant decrease in the number of holes, while the hole size appears to remain almost constant. Apparently, the reduction in overall free volume is achieved by some kind of process of diffusion, whereby free volume is both lost and at the same time distributed into regions of different local density.

The complexity of density fluctuations and of the associated free volume is further demonstrated by a careful study by Song and Roe\textsuperscript{108} of the effects of inducing volume changes in PS by various combinations of temperature and pressure histories as well as aging. The results are rather remarkable. They find, first, the not too surprising result that there are essentially no differences in the melt and glassy structures in respect of large-scale density fluctuations, or long-range ordering; it is the short-range structure (around 0.5 nm or smaller) which distinguishes the melt and glass. However, when examining this short-range structure following the various methods of achieving the given glassy state, they conclude that, on a 0.25–0.40 nm scale, physical aging enhances the short-range order, but that pressure densification actually reduces the short-range order. Thus it is possible to achieve states of lower volume with reduced short-range order. This surprising conclusion, which is supported by same “anomalous” results in cold-drawn PC,\textsuperscript{106} suggests that a re-appraisal of the usual concept of free volume and free volume distribution is appropriate.
3.7. Summary of Microstructural Aspects

The common theme running through all the above structural studies, both spectroscopic and scattering, is that the observations can in general be rationalised using the concepts of free volume and free volume distribution. In some instances, the correspondence between the results of the microstructural studies and the bulk volume relaxation is remarkable; for example, the fluorescence spectroscopic data of Royal and Torkelson\textsuperscript{90} on PVAc exhibit all of the features — asymmetry, memory effects, and the $\tau_{\text{eff}}$ paradox — of isothermal volume recovery. It seems particularly attractive, therefore, to invoke these concepts of free volume and its distribution in order to interpret the results. However, two questions remain.

First, what more about the glassy state can, or do, these microstructural studies reveal beyond confirming that the same phenomena are occurring on a macroscopic and microscopic scale? The answer must lie in the details of the processes, and in particular in a quantitative description of the free volume and its distribution. Significant advances have been made in this direction, by the use of selective labelling or probes of different size, for example, as discussed above. But at the same time, though, it is clear that in any quantitative analysis, experimental artefacts such as the radiation effects in PALS must not confuse the issue. It is most likely, therefore, that progress will be made by making use of the information available from a wide variety of techniques.

The second question arises because some of the observations, namely the SAXS data on cold-drawn\textsuperscript{106} and pressure densified\textsuperscript{108} glasses, cannot neatly be rationalised on the basis of free volume. It appears in these cases that some other kind of structural order becomes dominant when an external stress is applied to the material. The question, as was posed by Song and Roe,\textsuperscript{108} is whether the specific volume or the local structural order (or indeed, another parameter) is the more important in determining the properties of glassy materials. The volume has been a favourite for a long time, but there is a significant body of evidence to the contrary. This, of course, has important implications for changes in mechanical properties on aging, as will be discussed further below, where this question will be raised again. For the present, we note that it remains unanswered.

4. THEORETICAL TREATMENTS

4.1. Introduction

As has been discussed above, a popular interpretation of physical aging is in terms of the concepts of free volume and free volume distribution. Accordingly, we examine here the original free volume theory and its implications, and subsequent developments to include a distribution. These are essentially phenomenological developments, and have been widely applied to both volume and enthalpy relaxation. There are several shortcomings of these models, and two in particular are worthy of mention. First, it is clear from the SAXS data that free volume may not be the most relevant parameter to characterise aging; accordingly we introduce here, additionally, an
alternative approach in terms of configurational entropy. Second, the $\tau_{\text{eff}}$ paradox and the inability of these models to describe aging behaviour far from equilibrium have raised some doubts about the treatment of the non-linearity aspect of the relaxation, and indeed about the fundamental assumption of thermorheological simplicity. These are some of the aspects discussed in this section.

4.2. Free Volume

The concept of free volume originated from attempts to describe the variation of the viscosity $\eta$ of liquids above $T_g$, and is the basis for just one of several empirical equations proposed. The temperature dependence, for example, was proposed by Vogel, Fulcher and Tammann and Hesse in the form often expressed as:

$$\ln \eta = \frac{A}{T - T_0}$$  \hspace{1cm} (9)

where $A$ is a constant and $T_0$ is a temperature some distance below $T_g$. This is frequently referred to as the VTF equation.

An alternative empirical equation was later proposed by Doolittle, describing the viscosity in terms of the free volume fraction $f$:

$$\ln \eta = a + \frac{b}{f}$$  \hspace{1cm} (10)

where $a$ and $b$ are constants, $b$ being rather close to unity. The fractional free volume is defined as:

$$f = \frac{v - v_o}{v} = \frac{v_f}{v}$$ \hspace{1cm} (11)

where the free volume, $v_f$, is the difference between the actual volume, $v$, and an “occupied volume”, $v_o$.

A physical interpretation of eq. 10 was provided shortly thereafter by Cohen and Turnbull, the basis for their model being that molecular mobility requires a certain critical volume. This provided considerable respectability for the free volume theory, though it has never been without its detractors, largely because of a haziness about its definition, and in particular about what is meant by the occupied volume.

The temperature dependence of viscosity is introduced into this theory by assigning a thermal expansion coefficient to the free volume, and one of the remarkable strengths of the theory is that the famous WLF equation may be derived from it, and that the “universal” parameters of the model have physically reasonable values: the fractional free volume at the glass transition temperature is $f_g = 0.025$, and the expansion coefficient of free volume is $\alpha_f = 4.8 \times 10^{-4} \text{ K}^{-1}$. In fact, the VTF equation may also be expressed in WLF form, with the “universal” value of $T_g - T_0 = f_g / \alpha_f = 52 \text{ K}$. Another strength of the free volume theory is its conceptual simplicity, and it is probably this which has, as much as anything, maintained its popularity.
4.3. Configurational Entropy

One of the approaches towards resolving the Kauzmann paradox\textsuperscript{115} is to postulate a second-order thermodynamic transition at a temperature below $T_g$. The phenomena associated with aging in the transition region are observed because of retarded kinetics as time-scales for relaxation become longer, and it is not possible to observe this thermodynamic transition because the necessary equilibrium state would require an infinite time to be attained. Gibbs and Di Marzio\textsuperscript{116} used a lattice model to predict that the configurational entropy $S_c$ reduces to zero at a temperature $T_2$, somewhat analogous to the temperature $T_o$ in the VTF equation (eq. 9) where the viscosity becomes infinite. This configurational contribution to the entropy represents the number of configurations available to the polymer molecule, this number reducing as the temperature is lowered. Adam and Gibbs\textsuperscript{117} developed further these ideas with the concept of "co-operatively rearranging regions", units in which configurational changes can take place without influencing their surroundings, and derived an expression for the viscosity as:

$$\ln \eta = B + \frac{C}{TS_c}$$

where $B$ and $C$ are constants. By assigning a temperature dependence to the configurational entropy, it is possible to derive the WLF equation from this, in the same way as was possible for the VTF and free volume dependences.

4.4. Model of Moynihan, Hodge and Others

These concepts of free volume and configurational entropy, but particularly the former, have been the basis for a number of phenomenological models of volume and enthalpy relaxation. By relating the viscosity to a relaxation time $\tau$, it is simple to see how the required dependence of $\tau$ on both temperature and structure can be obtained: in eq. 10 the structure is defined through the fractional free volume, while in eq. 12 it is through the configurational entropy. In fact, a more common representation nowadays of the dependence of $\tau$ relies upon Tool's\textsuperscript{12} concept of fictive temperature, $T_f$, discussed earlier:

$$\tau(T, T_f) = \tau_o \exp \left[ \frac{x\Delta h^*}{RT} + \frac{(1 - x)\Delta h^*}{RT_f} \right]$$

where $\tau_o$ is the relaxation time in equilibrium ($T_f = T$) at an infinitely high temperature.

This equation is associated with the names of Tool, Narayanaswamy and Moynihan, though it was in fact Moynihan et al.\textsuperscript{36} who first expressed it in this way. It clearly separates the temperature and structure dependences, with the parameter $x(0 \leq x \leq 1)$ defining the relative contributions of temperature and structure to the relaxation time. Furthermore, the temperature dependence in equilibrium is of the Arrhenius type, with activation energy $\Delta h^*$. Although it is not immediately obvious, this equation is in fact equivalent to both the free volume and the configurational entropy dependences, and also to the WLF equation, when a
narrow temperature interval around $T_g$ is considered.\textsuperscript{118} Thus the non-linearity expressed by eq. 13 is a common feature of nearly all current models of relaxation kinetics.

Narayanaswamy’s name is associated with eq. 13 because he was the first to show\textsuperscript{119} how this non-linearity could be incorporated into the analysis of complex thermal histories. This involved the use of a “reduced time” which was a function of both $T$ and $T_f$, and of the way in which $T$ and $T_f$ had varied throughout the previous thermal history since the most recent equilibrium state.

The other requirement in this model is that there be a distribution of relaxation times. This can conveniently be achieved through the use of the stretched exponential response function:

$$\phi(t) = \exp[-(t/\tau)^\beta]$$

associated with the names of Kohlrausch,\textsuperscript{120} Williams and Watts,\textsuperscript{121} and hence referred to as the KWW equation.\textsuperscript{†} The exponent $\beta$ ($0 \leq \beta \leq 1$) is inversely proportional to the width of a corresponding distribution of relaxation times, and $\tau$ is given, for example, by eq. 13.

Equations 13 and 14 therefore introduce both non-linearity and a distribution to the model, albeit that the latter is in a somewhat arbitrary but mathematically convenient way. When combined with a constitutive kinetic equation, in which the isothermal rate of approach to equilibrium is proportional to the departure from equilibrium:

$$\frac{dT_f}{dt} = -\frac{T_f - T}{\tau(T, T_f)}$$

the model predicts the response of the system to any prescribed thermal history.

The pioneers of this model were Rekhson,\textsuperscript{123} Moynihan and co-workers,\textsuperscript{124} and Hodge and co-workers,\textsuperscript{43,45,125–128} and it has been remarkably successful in describing many of the characteristic features of structural relaxation, mainly isothermal enthalpy relaxation and DSC endotherms on heating at constant rate. The intention has really been to evaluate the parameters defining the kinetics ($x$, $\beta$ and $\Delta h^*$) for different polymer (and inorganic) glasses in order to examine the effect of chemical structure on the detailed relaxation process. In this respect, however, this approach has only been partly successful; there is quite a wide variation in the values of these parameters as a function of the experimental conditions (aging time and aging temperature, for example), as well as significant discrepancies between different research groups. A possible explanation\textsuperscript{129} lies in the fundamental assumption, inherent in this approach, to adopt a distribution of the KWW type, even though it may not be appropriate to such relaxations in all polymers. An alternative approach is afforded by the KAHR model.\textsuperscript{38}

\textsuperscript{†}This nomenclature (KWW) is used because Williams and Watts were, it is generally considered, the first to “rediscover” in 1970 the original idea of Kohlrausch from 1866. It is interesting to note, though, that ten years earlier, in 1960, Kovacs\textsuperscript{122} had utilised just such an expression to analyse the volume relaxation of polystyrene, and found an exponent $\beta$ (in fact Kovacs denoted the exponent as $n$) of approximately 0.5 at 80°C and increasing with temperature.
The KAHR model, developed by Kovacs, Aklonis, Hutchinson and Ramos,\textsuperscript{38} has the same foundation as those of Moynihan and others discussed above. The relaxation time has both a temperature and a structure dependence, which may be written for volume relaxation as:

\[ \tau_i(T, \delta) = \tau_{ir} \exp[-\theta(T - T_r)] \exp[-(1 - x)\theta \delta / \Delta \alpha] \]  

where \( \tau_{ir} \) is the value of \( \tau_i \) in equilibrium at the reference temperature \( T_r \), \( \delta \) is the relative departure from volumetric equilibrium, defined by eq. 1, and \( \Delta \alpha \) is the difference between the thermal expansion coefficient of the equilibrium liquid \( (\alpha_l) \) and of the glass of fixed structure \( (\alpha_g) \); the corresponding equation for enthalpy relaxation is:

\[ \tau_i(T, \delta_H) = \tau_{ir} \exp[-\theta(T - T_r)] \exp[-(1 - x)\theta \delta_H / \Delta C_p] \]  

where \( \delta_H \), the departure from enthalpic equilibrium, is defined by eq. 3, and \( \Delta C_p \) is the difference in the specific heat capacities of the equilibrium liquid \( (C_{pl}) \) and of the glass \( (C_{pg}) \). Equations 16 and 17 are identical to the Tool–Narayanaswamy–Moynihan eq. 13 over a limited temperature interval around \( T_g \),\textsuperscript{118} with an approximate equivalence between \( \theta \) and \( \Delta h^* \):

\[ \theta \approx \frac{\Delta h^*}{RT_g^2} \]  

The constitutive equation describing the relaxation kinetics is identical to eq. 15, but expressed in terms of \( \delta \) as:

\[ \frac{d\delta}{dt} = -\frac{\delta}{\tau(T, \delta)} \]  

with an equivalent expression for \( \delta_H \).

Thus far, all these models are essentially the same. The important difference between the KAHR model and those discussed earlier lies in the way in which the distribution of relaxation times is introduced. In the KAHR model, rather than using a continuous distribution of the KWW type, a discrete distribution is used. This is seen in eqs 16 and 17 where the subscript \( i \) refers to the \( i \)th element of a discrete distribution of \( N \) elements. Correspondingly, eq. 19a can be written for each element in the distribution as:

\[ \frac{d\delta_i}{dt} = -\frac{\delta_i}{\tau_i(T, \delta)} \]  

from which it can be seen that the model assumes a distribution \( \delta_i \), corresponding to the elementary values \( \tau_{ir} \). The sum of the elementary contributions \( \delta_i \) gives the total departure from equilibrium:

\[ \delta = \sum_{i=1}^{N} \delta_i \]
and the relaxation time distribution, in equilibrium at the reference temperature $T_r$, is defined by the set of paired values $(g_i, \tau_i)$, where $g_i$ is a weighting factor.

It should be noted that thermorheological simplicity is inherent in the above description of the KAHR model, since all the $\tau_i$ change with structure in the same way because it is the total $\delta$ which is included in eq. 16 (and the total $\delta_H$ in eq. 17). Indeed, this assumption of thermorheological simplicity is also inherent in all the models discussed earlier.

One of the advantages of the KAHR model over the others is its transparency; because of the use of a discrete distribution, it is possible to examine, at any stage during a relaxation process, the distribution of free volume (or $\delta_i$). This should not be confused with a change in the distribution of relaxation times; the relaxation time distribution defined by $(g_i, \tau_i)$ does not change in shape, according to the fundamental assumption of thermorheological simplicity. A schematic illustration of the change in the distribution of $\delta_i$ during isothermal relaxation is given in Fig. 5. Immediately after an instantaneous quench, the distribution of $\delta_i$ consists of equal $(g_i = 0.1)$ contributions from the ten elements (Fig. 5(a)). As the isothermal aging time increases, two things happen (Figs 5(b)–5(d)). First, the individual $\delta_i$ decrease in magnitude according to eq. 19a; because $\tau_1$ is the shortest relaxation time, it will relax during this short time
period by the greatest amount, while $\tau_{10}$ has hardly relaxed at all yet, and there will be
appropriate amounts of relaxation between these extremes. The total $\delta$ will decrease by
the sum of all the individual decreases of the $\delta_i$, and it is this value of $\delta$ which determines
the second effect, which is a shift along the log time scale according to eq. 16. Ultimately, the volume relaxation will be complete when all the $\delta_i$ have reached zero,
the longest timescale being determined by when element $\tau_{10}$ reaches equilibrium
($\delta_{10} = 0$).

Thus the multiparameter KAHR model allows the distribution of $\delta_i$ to be examined
at all instants during the relaxation. Relating this to a distribution of free volume, it
allows therefore a comparison with the observations from some of the spectroscopic
techniques discussed earlier, such as PALS and photochromic spectroscopy.

The application of the KAHR model also differs significantly from the approach
adopted by other workers, who generally attempt to fit the predictions of their
model to the DSC heating endotherm following various thermal treatments. As was
mentioned earlier, this requires the assumption of a distribution, almost invariably
the KWW function. The KAHR model approach, on the other hand, makes no
such assumption, nor does it attempt to fit the whole of the DSC curve. Instead,
it concentrates on examining the dependence of a characteristic feature of the DSC
endotherm, namely the peak endotherm temperature, on the experimental conditions,
in particular on the annealing time and sometimes on the heating rate. This is called
the peak-shift method.$^{37-40}$

The advantage of the peak-shift method is that it eliminates the need to make an
arbitrary choice of distribution. Since the limiting dependence of the peak temperature
$T_p$ on $\delta$ or $\delta_H$ is observed to be constant and largely independent of annealing
temperature over a wide range of experimental annealing times, the model appears
to be reliable, at least for aging at temperatures down to about 20°C below $T_g$,
and for both polymeric$^{37,59,60}$ and inorganic glasses.$^{130,131}$

4.6. Robertson–Simha–Curro Theory

The models discussed above, although they can be related to the physical concepts
of free volume, free volume distribution and configurational entropy, are essentially
phenomenological. In several instances, when curve-fitting procedures are adopted
in order to evaluate the parameters of the models, some physically unreasonable
values are obtained. This calls into question the usefulness of these models as far as
understanding the process of glassy state relaxation is concerned.

The Robertson–Simha–Curro (RSC) theory,$^{132}$ in contrast, attempts to model the
relaxation behaviour starting from a physical model of molecular relaxation events.
The theory originates from the earlier idea of Robertson,$^{133-135}$ to examine the
localised molecular re-arrangements involving different isomeric states. By consider-
ing a simple chain backbone with only two rotational states for each bond ($cis$ and
$trans$), and a relaxing environment described by a distribution of free volume resulting
from thermal fluctuations, his stochastic analysis gives quantitative agreement with
experimental data for isothermal volume relaxation following both “down” and “up”
temperature jumps. The RSC theory builds upon this by making use of an earlier cell model for free volume\textsuperscript{136} which allows a reduced equation of state to be written in terms of a free volume fraction.

The kinetics of volume change are derived from the stochastic model applied to the system in which the relaxing species do so in an environment of free volume distributed according to a binomial distribution. Some of the assumptions of the model are: that the rate of change of free volume in a local region is a function of the free volume in that region; and that the transition from one state to another within a region depends not only on the free volume of that region but also on the surrounding regions, to a greater or lesser extent depending upon a parameter $z$. It is particularly interesting to observe that these assumptions are very similar to those contained within the KAHR model; the first assumption is implicit in eq. 19b, and the second in eq. 16, though in the KAHR model the parameter $z$ is effectively infinite, since the relaxation time for each region is influenced not just by the neighbouring regions but by the global free volume.

The agreement between theory and experiment is quite good\textsuperscript{132} for single temperature jumps, both down and up, with what are claimed to be physically meaningful values for the parameters, though the fractional free volume at $T_g$ for PVAc seems very high. A particularly interesting feature is that the results of the model begin to approach the "anomalous" behaviour associated with the $\tau_{\text{eff}}$ paradox\textsuperscript{14}. The explanation lies in the way in which the regions of very low free volume fraction approach equilibrium only very late in the relaxation, and the detailed predictions in this region are strongly influenced by $z$, the parameter which relates the local relaxation behaviour to its environment. In the KAHR model, this was treated simply by a mean-field approach, and must be an over-simplification. The RSC theory seems to provide a better means of allowing for this interaction, whilst also giving a physically more meaningful picture.

It must be said, though, that there are still significant differences between the RSC theory and experiment, particularly in the final region of the relaxation where the $\tau_{\text{eff}}$ paradox becomes apparent. The only approach which, to date, has really successfully described this region is the coupling model, discussed below.

### 4.7. Coupling Model

This model was originally proposed by Ngai\textsuperscript{137,138} some fifteen years ago, and has subsequently been applied to several aspects of relaxation processes. The essential feature of the model is that it treats the co-operativity between regions of a dynamically relaxing system in a different way from other models. The argument\textsuperscript{139} is that the relaxation of a "primitive species" is not isolated from its surroundings, and the strength of the coupling of this primitive species to its environment is determined by a parameter $n$ ($0 \leq n \leq 1$), the strength of the coupling increasing with $n$.

Thus, although the relaxation of the primitive species may be described by a time-independent rate $W_o = \tau_o^{-1}$, this rate is modified by the interaction of the primitive species with its surroundings to give a time-dependent rate $W(t)$. On timescales for
which $\omega_C t \gg 1$, where $\omega_C$ is a critical frequency, typically of the order of $10^{10}$ s$^{-1}$, the relaxation function $\phi(t)$ can be described by the rate equation:

$$\frac{d\phi}{dt} = -W(t)\phi$$

(21)

This can be integrated to give the function:

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau^*}\right)^{1-n}\right]$$

(22)

where $\tau^*$ is a “coupled” relaxation time expressed as:

$$\tau^* = \left[\frac{1}{(1-n)\omega_C^2 \tau_0^*}\right]^{1/(1-n)}$$

(23)

There are several implications of this coupling model, one of which is that it predicts a stretched exponential (KWW) decay function, as can be seen by a comparison of eqs 22 and 14, in which the exponent $\beta$ is identified as $(1-n)$. Thus strongly coupled systems have low values of $\beta$ and an apparently broad distribution of relaxation times. This prediction, ab initio, of the stretched exponential response function is considered to be one of the strengths of the coupling model.

Another implication, and one that sets the coupling model apart from others, is that the parameter $n$ need not be constant during a relaxation. The model is therefore not thermorheologically simple, which is a basic assumption of the models discussed earlier above.

In the present context, it is in particular this latter implication which is interesting in respect of the application of the coupling model to isothermal volume relaxation. By allowing $n$ to depend upon both temperature and structure, $n(T, \delta)$, this model is able to describe the expansion gap of the $\tau_{eff}$ paradox, and in such a way as to provide rather good agreement with the experimental data of Kovacs, a feat which is not achieved by any other model.

Furthermore, it is also able to predict the apparently anomalous finding of Bero and Plazek that, at rather slow cooling rates, all the cooling curves for their epoxy resin appear to reach an asymptotic glassy state at about the same temperature; the thermorheologically simple (or so-called reduced time) models cannot explain this behaviour.

These are significant achievements in the explanation of some characteristic features of relaxation kinetics. A note of caution must be sounded, though, since these experiments which have been successfully modelled represent only a limited number of those which are commonly used. Most particularly, the question remains of how well the coupling model can predict the response of a glassy system to a constant heating rate, which is typical of DSC experimental data. Until recently, the answer was that the coupling model showed an anomalous behaviour under such circumstances, such as an uncharacteristic undershoot following the endothermic peak; now, though, it is realised that these anomalous results emerged from an incorrect analytical procedure. It remains to be seen, therefore, whether the coupling model will have a more general application in its description of relaxation phenomena, or whether its success will remain limited to certain specific circumstances.
4.8. **Summary of Theoretical Aspects**

There are a number of important conclusions which may be drawn from a consideration of all of the models discussed above.

They all incorporate the two aspects of non-linearity and non-exponentiality (or distribution of relaxation times) which have long been recognised as essential. In this way, they all provide at least a qualitatively good description of many relaxation phenomena. The details of the ways in which these aspects are introduced is obviously different between the models, for example free volume versus configurational entropy, or continuous KWW versus discrete distribution functions, but these differences are of relatively minor importance in comparison with their common features.

The most important of these common features, and probably the key to the development of a model which is both physically realistic and successful in its predictions, is the recognition of an incorporation of co-operativity into the analysis. Indeed, this idea was already present in the configurational entropy theory of Adam and Gibbs, who introduced the concept of co-operatively re-arranging regions. The assumption of a mean-field approach is inherent in the models of KAHR and Moynihan and others, though it is most clearly evident in the former; each element in the distribution relaxes on a timescale which is influenced by the global environment. A modification of this assumption, on the basis of a molecular model, was introduced by the RSC theory. Here, the effect of the surroundings on the transition kinetics in any region is determined by a parameter $z$, which has a rather sensitive influence on the detailed relaxation behaviour. And finally, the coupling model refines this further by means of the parameter $n$, which now may depend upon the structural state; thus the interaction of microscopic regions with their surroundings is continuously varying throughout the relaxation.

This concept of co-operativity therefore runs as a common thread through all of these analyses, and is emerging as the corner-stone of any theory. It is anticipated that much attention will be focused in this area, and it is likely that microstructural experimental data from spectroscopic and scattering techniques will be particularly revealing.

5. **The Effects of Physical Aging on Mechanical Properties**

5.1. **Introduction**

The previous sections have shown clearly that the state of the glass is strongly influenced by its thermal history, and that this effect is evidenced by both the bulk response (volume and enthalpy) and detailed changes in the microstructure. In the simplest case, when an amorphous polymer is cooled from above to below $T_g$ and the temperature is thereafter held constant, the approach to equilibrium of the glass, which has excess thermodynamic quantities, involves an ever lengthening timescale as the molecular mobility is continuously reduced. As discussed, this may be
interpreted in terms of a reduction of free volume or configurational entropy, or as an increased coupling of the relaxation mechanisms to their environment.

It is to be anticipated that these structural changes on aging will have an influence on any property which is a function of molecular mobility, in other words on any viscoelastic property. Of particular interest here is the effect of aging on the mechanical viscoelastic response, which is characterised in the low strain (linear) region by the creep compliance, the stress–relaxation modulus or the dynamic mechanical properties (complex modulus and loss tangent). Such studies have formed the foundations upon which an extensive phenomenology has been built, particularly in the last 15 years or so. There is widespread agreement about virtually all the qualitative aspects of such physical aging effects, but, surprisingly, quantitative analyses still arouse some controversy, which stems from differing viewpoints about some of the most fundamental assumptions. This topic is examined in some detail immediately below.

In addition to the low strain, linear viscoelastic response, the non-linear response is also affected by aging. Indeed, this is no less important in engineering terms since properties such as yield stress and the question of whether deformation will be ductile or brittle (by shear yielding or crazing mechanisms, respectively), for example, are sensitive to the aged state of the material. The situation here is considerably more complex than for the linear response, since there is the possibility, even the likelihood, of the interaction of the applied stress with the aging process. This is an area in which many different opinions are currently held, and a summary of the contrasting ideas is given below.

Finally, the aging behaviour of semi-crystalline polymers poses some interesting questions, which seem to challenge the fundamental hypotheses relevant to the physical aging of amorphous polymers. This is just one further obstruction to the formulation of a generally accepted theory which can link together the structural changes occurring during aging in polymers with the changes in their mechanical properties. Nevertheless, as will be shown, whilst there is certainly not any universal agreement, many theoretical treatments can describe rather well the observed behaviour, and have strong predictive capabilities.

5.2. Phenomenological Aspects

The first reference in the literature to the physical aging of mechanical properties is in a brief note by McLoughlin and Tobolsky, who report the effect of the rate of cooling on stress relaxation of PMMA; when the polymer was cooled more slowly from above \(T_g\) to 80°C, stress relaxation occurred much less rapidly than for a quenched sample. This difference was attributed to a smaller decrease in specific volume for the faster cooled sample. Thus the qualitative link between aging of mechanical properties and volume relaxation was made for the first time.

It was some time before this attribution was repeated. In 1963, Kovacs et al. investigated the dynamic mechanical properties of PVAc in the glass transition region, and observed a correspondence between the volume relaxation behaviour and the changes in complex modulus and \(\tan \delta\), both types of experiment being made in parallel, during isothermal annealing at a range of temperatures just below \(T_g\).
After thermal equilibrium had been established following a quench, the storage modulus $G'$ was seen to increase approximately linearly with log time, while tan $\delta$ decreased almost linearly, when the volume approached equilibrium by contraction. On the other hand, during volume expansion, $G'$ decreased and tan $\delta$ increased, and the kinetics for both was observed to be autocatalytic, as for the volume. These changes were attributed to the isothermal relaxation of free volume, and interpreted in terms of a shift of the mechanical relaxation spectrum along the log time or log frequency axis with changes in free volume. It should be noted, though, that these authors were unable to superpose the data for the loss modulus, $G''$, at long aging times; further reference will be made to this later.

At about the same time Turner, in one of a series of papers describing creep in thermoplastics, observed a thermal history effect in unplasticised PVC.\textsuperscript{147} The results are reproduced in Fig. 6, where it can be seen that the creep curves at increasing times of storage at 60°C appear to be shifted towards longer creep times. Turner noted, in addition, that storage at 70°C produced a greater effect than at 60°C, and that a short heating period 80°C eliminated the effects produced by 12 weeks storage at 60°C. Without apparently being aware of the work of either McLaughlin and Tobolsky\textsuperscript{145} or Kovacs et al.\textsuperscript{146} Turner interpreted his observations in terms of a reduction of free volume during a storage period below $T_g$, noting additionally that the effects would be enhanced by rapid cooling.

These early reports are interesting particularly in that they capture the essence of the large body of work which has followed in more recent years: first, that the effect of aging is apparent as a shift of timescale of the mechanical response; second, that the results may be interpreted in terms of free volume; and third, that if one looks rather closely at the data, there are often deviations from the ideal behaviour described by a simple shift of timescale. But the major work on physical aging, and the one which has provided the reference for all subsequent research, is the extensive work done by Struik between 1962 and 1976 at the Centraal Laboratorium TNO in Holland, and published

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**Fig. 6.** Effect of thermal conditioning treatment on the tensile creep of rigid PVC at 60°C under a stress of 2.0 MPa. Durations of storage at 60°C were: (A) 1 h; (B) 4 h; (C) 17.5 h; (D) 72 h; (E) 168 h; (F) 2016 h (reproduced from ref. 147, with permission).
in 1978 as ref. 16, though selected parts were published separately earlier. The main aspects of physical aging are best summarised with reference to this work, and with reference to the low strain creep response in particular.

First, it is important to recognise that the aging process, by which the structural state is changing, is occurring continuously in the glassy state. If the creep response is to be used to monitor the aging, then the duration of the creep test must be short with respect to the aging time, in order that the glass may be considered to be in an isostructural state throughout the creep test. The usual procedure is to allow creep for a maximum of one tenth of the aging time. With appropriate allowance for a sufficient recovery period between each creep test, this imposes some experimental limitations which must be respected if the results are to be interpreted unambiguously. Note that the data shown in Fig. 6 do not follow this scheme.

A typical result from Struik's work\textsuperscript{148} is reproduced in Fig. 7, showing the creep compliance at low strain (0.3%) as a function of creep time for rigid PVC which has been quenched from above $T_g$ to 40°C and aged at 40°C for the times indicated. The most obvious feature here, as in Fig. 6, is the shift of the creep curves to longer times as the aging proceeds. It is often claimed that time--aging time superposition can be achieved by shifting the curves, and the arrow in Fig. 7 indicates the shift direction (almost horizontal) for which optimum superposition can be achieved. Good superposition, though, is not always achievable, and apparently superposable creep curves may, on closer inspection, not superpose well. For example, the data of Struik for the aging of PVC, reproduced here in Fig. 7, do not actually superpose to form the master curve shown when the indicated horizontal shift is used; the reason for this is not clear.
Furthermore, the shift required is not always horizontal; vertical shifts, usually downwards with increasing aging time, are also often required. Some implications of these aspects are discussed in the next section.

The amount of horizontal shifting along the log timescale (log $a$) is a function of the logarithm of the aging time (log $t_a$), from which a double logarithmic shift rate $\mu$ is defined:

$$\mu = \frac{d \log a}{d \log t_a}$$

It is a rather remarkable fact that this shift rate $\mu$ turns out to be very close to unity for all amorphous polymers in the temperature range just below $T_g$, falling rapidly towards zero (no aging) above $T_g$ and decreasing more slowly from unity as the temperature is reduced further below $T_g$. According to Struik, $\mu$ tends to zero as the $\beta$-relaxation region is approached, so that aging apparently ceases in the region of the secondary transition, but this has been disputed by several workers. It should be pointed out that the value of $\mu$ will depend upon whether or not a vertical shift is applied in order to superpose the data; this will be considered further below.

We note in passing that Struik has pointed out that this behaviour, namely superposition of creep curves by a more or less horizontal shift along the timescale, is a rather universal phenomenon. He caused some considerable amusement at the conference on Yield, Deformation and Fracture of Polymers at Churchill College, Cambridge, in March 1976, when he presented the aging behaviour in creep of a variety of materials including Dutch cheese!

The aspects of physical aging discussed above suggest that there is a correlation between the specific volume and the changes in the creep compliance. Results such as those presented in Figs 6 and 7, though, correspond only to isothermal volume contraction. A more demanding test of the validity of this correlation is afforded by more complex thermal histories such as those shown schematically in Fig. 8. Kovacs was the first to show that the time evolution of $\delta$, initially in apparent equilibrium at $T_E$ (Fig 8(a)), displays a "memory effect" and passes through a maximum before returning to a true equilibrium at a longer time. If there is a direct correlation between volume and the aging of mechanical properties, then one would anticipate, for these thermal histories, an initial shift of creep curves in the direction of shorter times, as the value of $\delta$ increases, followed by the more usual shift to longer times as $\delta$ decreases towards zero again. Struik has shown that this is indeed the case for a wide range of polymers including PS, PC and rigid PVC, from which he concludes that, on aging, the mechanical creep behaviour shifts along the timescale by an amount determined uniquely by the momentary value of $\delta$ (or of the specific volume).

The majority of Struik's aging studies of mechanical properties have involved creep. Other techniques that have been used include, in particular, stress relaxation and dynamic mechanical analysis, and it is instructive to examine some reported effects of aging on these aspects of mechanical response. In all cases, it is found that the stress relaxation curves of a wide variety of polymer glasses including PMMA, PS, epoxy, PMMA blends, and rigid PVC can be superposed by means of a horizontal shift along the log timescale. Often an additional vertical
Fig. 8. (a) Schematic illustration of thermal cycles used to produce memory effects in dilatometry\textsuperscript{14} and mechanical creep response\textsuperscript{15,19}. From an equilibrium state at A, the polymer is cooled and then annealed at a temperature in the glassy state (\(T_n, T_C, T_D\)) for a length of time such that when reheated to temperature \(T_E\) the volume will be equal to the equilibrium value. (b) The time evolution of \(\delta\) (eq. 1) on aging at temperature \(T_E\) having followed each of the paths (ABE, ACE, ADE) in (a) to reach state E.

shift\textsuperscript{150,152,154} is required, though in the work of Mijovic \textit{et al.}\textsuperscript{155,156} it is not possible to determine whether any vertical shifting has been used, since the data have been normalised to the initial value of the stress relaxation modulus. The question of the validity or otherwise of applying a vertical shift to the data is considered in more detail below, but it clearly has an effect on the shift rate \(\mu\), and hence on the interpretation of the data. A further difficulty arises because of the strain values employed; in all of these experiments apart from those of Lee and McKenna,\textsuperscript{152,154} the applied strain was at least 0.5\%, and occasionally as large as 1.0\% or more,\textsuperscript{153} which must raise some doubts about whether or not the material is in its linear viscoelastic region. Possible interaction of the applied strain (or stress) with the aging process is an area of current controversy, and is examined in a later section. The interpretation of these data must therefore be tempered with a little caution on both the above counts. Nevertheless, the general picture that emerges from these stress relaxation studies is the same as that from creep studies: that the major effect of physical aging is a shift in timescale, and with a shift rate \(\mu\) that is close to unity when the aging temperature is not too far below \(T_g\). Interestingly, Vleeshouwers \textit{et al.}\textsuperscript{153} find the same value of \(\mu\) for epoxy in both creep and stress relaxation, while the creep relaxation time is significantly greater than that for stress relaxation. However, the relative magnitudes of creep compliance and stress relaxation modulus deviate from the predictions of linear viscoelastic theory,
and one must conclude, as intimated above, that the epoxies are in a nonlinear regime, thus making quantitative analysis difficult.

The alternative technique of dynamic mechanical analysis (DMA) or dynamic mechanical thermal analysis (DMTA) has also been used to study physical aging. In the early work of Kovacs,\textsuperscript{146} and of Meyer, \textit{et al.},\textsuperscript{158} for example, a torsion pendulum was used, involving free vibrations, whereas modern instruments nowadays use forced oscillations over a quite wide range of frequencies. The distinction is not trivial. With forced oscillations, particularly at temperatures close to the transition region, where $\tan \delta$ can reach rather large values (>1), it becomes difficult for the material to dissipate the energy input due to the testing. This can lead to internal heating of the sample, or to other interactions of the deformation with the structural state of the material, which will distort the response.

The other significant feature of DMTA instrumentation is that it offers a constant heating rate mode, as in DSC, and, perhaps as a consequence, this is the mode that is rather commonly used in studies of physical aging by DMTA (e.g. see refs 57, 159–161). Unfortunately, this is not the mode in which the results are most easily amenable to interpretation. The reason is that during the heating scan the structure of the sample is continuously changing, and in a rather complex way that depends upon, in particular, both the annealed state of the sample prior to heating and also the heating rate. In DSC, of course, the same situation prevails, and it is well known that this can give rise to complex features in the DSC trace,\textsuperscript{162} including “sub $T_g$” peaks\textsuperscript{163} and “upper peaks”\textsuperscript{164} in addition to the usual annealing features.

Nevertheless, we can review some of the important findings from dynamic mechanical studies of aging in polymers. In particular, the early work of Petrie\textsuperscript{165,166} made use of a torsion pendulum and examined the isothermal evolution of properties. Petrie claims a correspondence between the evolution of dynamic mechanical properties and of enthalpy in PS, following both “down” and “up” quenches, in other words when equilibrium is approached from a state having either excess or deficient thermodynamic properties. Some of these results are included in a review by Tant and Wilkes,\textsuperscript{167} where the storage modulus is seen to increase and the logarithmic decrement decrease during isothermal annealing of PS at 92°C following a down quench. Despite the fact that these data are plotted versus linear time rather than logarithmic time, it is possible to see that these mechanical properties reach an equilibrium state, if anything at an earlier time than does the enthalpy. In as much as it is generally believed that volume relaxation occurs on a shorter timescale than does enthalpy relaxation, this suggests that the evolution of mechanical properties follows the volume, as suggested by Struik.\textsuperscript{168,149}

These time dependent changes in dynamic response observed by Petrie in PS have been confirmed by several other workers who have studied the isothermal behaviour following a quench. For PMMA annealed both just below\textsuperscript{21} and far below $T_g$ after quenching from above $T_g$, $\tan \delta$ is observed to decrease with log aging time, while the storage modulus $E'$ increases. Indeed, according to Perez \textit{et al.}\textsuperscript{21} the mechanical properties $E'$ and $\tan \delta$ approach equilibrium at a faster rate than does the volume recovery, which itself is faster than enthalpy recovery. In a similar study of some
polystyrene blends, \( E' \) increases while the loss modulus \( E'' \) decreases monotonically during isothermal aging at a temperature about 15°C below \( T_g \). Following more complex thermal histories, memory effects similar to those seen originally by Kovacs in volume relaxation and later by Struik in creep have also been observed in \( E' \), \( E'' \) and \( \tan \delta \) thus confirming an apparently close correspondence between dynamic mechanical properties and the structural state of the glass, as evidenced for example by its specific volume.

A brief mention should also be made of torsional braid analysis (TBA), which is an automated torsion pendulum alternative to conventional DMTA. The TBA technique measures the logarithmic decrement and a quantity known as the relative rigidity, which is proportional to the modulus \( E' \). Isothermal aging studies of epoxy resin by TBA have shown the usual characteristics, namely an increase in \( E' \) and a decrease in logarithmic decrement as a function of aging time following a quench or a slow cool from above \( T_g \).

### 5.3. Time-Aging Time Superposition

It has been shown above that the major effect of aging on the mechanical properties measured by creep and by stress relaxation is a shift in the timescale to longer times on isothermal annealing, for the most commonly used thermal history involving a quench from above to below \( T_g \). This effect is manifest as a shift of the creep or stress relaxation curves along the log time axis. It is tempting, therefore, to attempt to analyse this behaviour by examining the superposition (or otherwise) of these curves for different aging times by a procedure analogous to that suggested many years ago by Leaderman for time-temperature superposition. It is, in fact, rather remarkable that this technique of time-temperature superposition has enjoyed, and continues to enjoy, such success as it has, in the light of these observations about the effects of physical aging. The superposition of creep and stress relaxation data at different temperatures, particularly in the region just below \( T_g \) but to a certain extent at all temperatures, must be subject to shifts due to aging, and will result in erroneous time-temperature shift factors unless this is taken into consideration.

There is no doubt that time-aging time superposition can be achieved for the large majority of published data to a greater or lesser extent. When examined in detail, however, numerous deviations from this simple procedure are observed. In the work of Struik, for example, which has laid the foundations for most subsequent aging studies, one can already begin to see the difficulties. The problem is that, whilst the main effect of aging is a horizontal shift along the log timescale, optimum superposition of his creep data is achieved often by means of additional vertical shifts. This applies not only to the data of Struik, but to published data on aging in general. When the creep data are rather flat and with only small curvature, any vertical shifting will have a significant effect on the extent of horizontal shifting to obtain good superposition, and hence on the magnitude of the double logarithmic shift rate \( \mu \). The quantitative analysis of aging by this approach is therefore compromised.
In fact, there is a possible justification for applying vertical shifts, but the procedure needs to be examined in some detail, as was demonstrated by Chai and McCrum. Their argument is explained briefly with the aid of Fig. 9. Suppose that, on aging, the creep curve is not only shifted to longer times horizontally, but that also both the unrelaxed \( J_U \) and relaxed \( J_R \) compliances change (and hence also the relaxation strength, \( \Delta J \)). It is clear from Fig. 9 that in general it will not be possible to superpose the unaged and aged creep curves, even using a vertical shift. Chai and McCrum analysed this situation using the parameters \( b \) and \( c \) to characterise the aging time dependence of \( \Delta J \) and \( J_U \), respectively, with the horizontal shift log \( a \) determined by the shift factor for the timescale, \( a \). These parameters are analogous to those used previously by McCrum and Morris to allow for similar effects in time–temperature superposition, and can be written as:

\[
\Delta J^b = b \Delta J^a \tag{25}
\]

\[
J_U^b = c J_U^a \tag{26}
\]

where the superscripts \( a \) and \( b \) refer to the unaged (a) and aged (b) curves, respectively, in Fig. 9.

It can be seen that horizontal shifting alone will be valid only if \( b = c = 1 \), while horizontal plus vertical shifting will effect superposition only when \( b = 1 \). Thus the majority of conventional analyses of aging of mechanical relaxation data, which utilise horizontal plus vertical shifting, make the rather drastic assumption that \( \Delta J \), the relaxation magnitude, is unaffected by aging. In our view, not enough attention has been paid to this point, particularly as Chai and McCrum proposed a procedure to eliminate the effects of the parameter \( c \). This procedure examines the curves of creep rate \( dJ/dt \) plotted on a logarithmic scale, as a function of log time, which should superpose for a thermorheologically simple system with a horizontal shift of log \( a \) together with a vertical shift of \( (\log a - \log b) \). Besides the work of McCrum very few other studies of aging have made use of this approach.
The need to take into consideration the changes in the limiting compliances as a function of aging has been demonstrated very clearly by Read and co-workers.\(^{180-184}\) By using a combination of static and dynamic techniques they were able to cover a very wide range of times, from \(10^{-8}\) to \(10^{5}\) s, and thus include the secondary \(\beta\) transition in addition to the \(\alpha\) glass transition of amorphous polymers. This analysis has shown that physical aging reduces the magnitude of the \(\beta\)-relaxation process in PMMA,\(^{180}\) PC,\(^{181}\) and PVC,\(^{183}\) and hence reduces the unrelaxed compliance for the \(\alpha\) relaxation glass transition region. More importantly, when the \(\alpha\)- and \(\beta\)-relaxation regions overlap significantly, as is the case for PMMA,\(^{180,182}\) it will become impossible to superpose the creep data for different aging times in the \(\alpha\)-relaxation region, and particularly so for short creep times.

When the creep data in the \(\alpha\)-relaxation region are separated from the effects of the \(\beta\)-relaxation, superposition of the data for different aging times can be achieved, but it is not possible to distinguish, from short-term data, whether aging involved changes in timescale, or \(\Delta J\), or both.\(^{182}\) A constant value of \(\Delta J\) on aging was preferred, however, in order to obtain a good fit to long-term data.

The conclusion from the work of Read and co-workers is therefore that the \(\alpha\)-relaxation strength remains constant on aging \((b = 1)\), and that superposition can be achieved by horizontal and vertical shifting \((c < 1)\). The implication is that the behaviour is thermorheologically simple, in other words that the relaxation time spectrum remains unchanged on aging. This is not the conclusion reached by McCrum and co-workers from their analysis of physical aging of creep in both polypropylene\(^{175}\) and an amorphous polymer, a cross-linked co-polymer of acrylonitrile and butadiene.\(^{185}\) They found that they were unable to superpose the data, even when allowance was made for the possibility of vertical shifting, and concluded that the relaxation spectrum changed shape during aging. This is a major departure from the usual assumption of thermorheological simplicity, and has led to the proposal of "sequential aging" as an interpretation of their results\(^{185,186}\) particularly in the light of some "thermal sampling" experiments. The basic hypothesis of sequential aging is that, at any time during the aging process, only a small part of the spectrum of relaxation times is contributing to the aging. Specifically, at short aging times only those times in the creep relaxation time spectrum of the same approximate magnitude as the aging time are influenced by the aging. At longer aging times, these short creep relaxation times will be in equilibrium, while longer times within the creep spectrum, which are again of the same order of magnitude as the aging times, will now represent the active mechanisms and will be affected by the aging. Thus the effects of aging move sequentially through the creep relaxation time spectrum.

This sequential aging process can be described mathematically, in a simple but rather revealing way, and compared with the volume relaxation process, by means of the multiparameter KAHr model.\(^{38}\) For volume relaxation, the evolution of \(\delta\) with time is found from eqs 19b and 20, as the sum of a number \(N\) of elements \(\delta_i\), each of which has an associated relaxation time \(\tau_i\). The important point here is that all \(\tau_i\) depend upon the total value of \(\delta\) (eq. 16), and not upon the individual values of \(\delta_i\); this is the origin of the thermorheological simplicity of the model.
Consider now the creep compliance, which can be written, in a corresponding discrete form as:

\[
J(t) = J_U + \sum_{i=1}^{N} \Delta J_i [1 - \exp(-t/\tau_{ic})]
\]

where the spectrum of creep relaxation times \(\tau_{ic}\) is composed of \(N\) elements; to simplify the argument, this value of \(N\) has been chosen to be identical to the number of elements in the volume relaxation time spectrum, but this is not an important aspect. Ignoring variations of \(\Delta J_i\), with increased aging time the creep relaxation times \(\tau_{ic}\) will increase, and the creep compliance curves will shift to longer times. If, by analogy with the volume relaxation KAHR model, each \(\tau_{ic}\) is the same function of the total \(\delta\), then all elements in the \(\tau_{ic}\) distribution will shift simultaneously by the same amount; thus the creep curves will be superposable, and the behaviour is thermorheologically simple.

On the other hand, sequential aging would associate each \(\tau_{ic}\) with a corresponding element \(\tau_i\) of the same magnitude in the volume relaxation time spectrum. More particularly, each \(\tau_{ic}\) will depend upon the individual \(\delta_i\) elements. Since the \(\delta_i\) relax sequentially (see Fig. 5), this implies that the creep response will likewise age sequentially. Furthermore, the behaviour will be thermorheologically complex.

How are these opposing views to be reconciled: does the relaxation time distribution change shape on aging or not? One point to note is that, examining the evolution of the elements \(\delta_i\) in Fig. 5, one might be led to believe that a sequential aging process is occurring in volume relaxation. In a sense it is, in as much as the individual elements \(\delta_i\) are indeed relaxing sequentially. However, this is simply the observed result of the interaction of the relaxation kinetics with the spectrum; the effect of the aging on the spectrum itself, as is clearly shown in Fig. 5, remains a shift of the entire spectrum, without change in shape, to longer times. This, of course, is a fundamental assumption of the KAHR model.

We offer the suggestion that the "thermal sampling" experiments can be misleading in the same way: the observed response appears to relax sequentially, but the underlying effect on the relaxation time spectrum is a shift of the entire spectrum without change in shape. This idea remains to be examined theoretically, but we note that the correspondence of individual elements of the creep relaxation time spectrum with individual elements of the volume relaxation time spectrum seems contrary to intuition. One would, in particular, anticipate an influence of the surrounding environment on the individual relaxation times, this idea of co-operativity being considered increasingly important nowadays in our attempts to understand glassy state relaxation. Indeed, the emergence of the coupling model has this idea at its heart.

On the other hand, the reasons for the discrepancies may be more mundane. The ability or otherwise to superpose creep or stress relaxation data at different aging times relies, to a certain extent, on a subjective judgement of goodness of fit. Furthermore, the array of possible extraneous factors that can modify the course of the relaxation and aging behaviour is considerable: duration of creep or stress relaxation test with respect to aging time; magnitude of stress or strain level and possible interaction with
aging process (see below); possible changes in limiting compliances or moduli; provision of sufficient recovery time between repeated tests. In spite of all these potential complications, it is rather remarkable that the effect of physical aging appears, in general, to be well described as a shift of the whole relaxation time spectrum without change in shape, and with a relaxation strength that remains essentially constant with age.

There is one particular area, though, in which it is common to see significantly different behaviour from that described above, and this is when there is an interaction between the test itself and the aging process that the test is probing. Such interaction occurs when the stress level in creep or the strain level in stress relaxation is large, and is the subject of the following section.

5.4. Interaction of Applied Stress/Strain with Aging

All of the results and discussion in the previous section apply (or are intended to apply) to the linear viscoelastic region, at stresses or strains sufficiently low so that one can assume that the test itself (creep or stress relaxation or dynamic mechanical testing) does not significantly modify the structural state of the material. At higher stresses it is likely that the material will be in the non-linear viscoelastic region, and additionally that there will be an interaction between the applied stress or strain and the glassy structure. Indeed, as we shall see, it has been argued that the non-linear viscoelastic response is a result of this interaction, and hence that non-linearity and physical aging are inextricably bound together. This particular aspect of physical aging, perhaps because of its inherent complexity, has been the realm of some considerable controversy, and the situation is far from being resolved.

The earliest reports of this interaction were made by Sternstein and co-workers,187-189 who observed what they called a "mechanical enhancement" of aging in the stress relaxation of PMMA in uniaxial tension at 30°C. Their results are reproduced in Fig. 10. It seems that each successive stress relaxation curve following the quench is approaching the slowly cooled curve in the usual manner. However, when \( Q(I) \) was repeated after an aging time of 9000 min rather than 900 min, the response was almost identical to \( Q(I) \) in Fig. 10, and the subsequent three cycles were indistinguishable from those shown. Similar results were obtained for plasticised and unplasticised PVC and for PC at similar strain levels. Evidently the aging time itself is having a negligible effect in comparison with the mechanical history.

Before examining why these results are possibly controversial, it is worth noting some experimental details. First, as given in the caption to Fig. 10, the recovery period between each stress relaxation test is only 1000 min, in comparison with a 500 min duration for the test itself. This would certainly not be sufficient time for full recovery to occur. Second, one would expect the response of a quenched and annealed sample to approximate that of a slow-cooled sample when the annealing time is long, as is the case for the repeat \( Q(I) \) test. Here the annealing time was 9000 min and \( T_g - T = 90°C \), so that the thermal history might be considered equivalent approximately to a cooling rate of 0.01°C/min. The slow-cooling rate is not specified...
Fig. 10. Repetitive cycle stress relaxation at 0.5% strain in PMMA for quenched (Q) and slow cooled (SC) samples. The repetitive cycles were made as follows: quench from above \(T_g\) to 30°C, age 900 min; Q(I), recovery for 1000 min; Q(II), recovery for 1000 min; Q(III), recovery for 1000 min; Q(IV). Each stress relaxation test is of duration 500 min (reproduced from ref. 189, with permission).

In any of refs 187–189, but it is unlikely to be much slower than 0.01°C/min. And yet Q(I) and the slow-cooled curve in Fig. 10 are separated by almost 1.5 decades on the timescale. These considerations indicate some of the difficulties in the interpretation of such data.

In contrast to these results suggestive of mechanical enhancement of aging, and what makes them controversial, the results of Struik\textsuperscript{16} as well as others, are indicative of a kind of "rejuvenation" under high stresses. This is exemplified not only by a reduction in shift rate \(\mu\) as stress level increases,\textsuperscript{16} but also by the observation that a high stress "pulse" in the midst of the usual small strain creep tests, such as are shown in Fig. 7, acts to shift the creep response to shorter times, whereupon physical aging commences again in the usual way.\textsuperscript{16,190,191}

An explanation for this apparent contradiction between the results of Sternstein and co-workers and Struik has been given by Struik,\textsuperscript{192} which may be summarised as follows, with reference to Fig. 11. At low strains, creep curves at increasing aging times shift to longer times in the usual way; this occurs in an identical way whether the creep curves are measured in a single sequence following the quench (the procedure most often adopted, and labelled Type 1 by Struik), or whether a new quench and aging time is made for each test (Type 2). For high stress experiments, the action of the mechanical stress is to rejuvenate the sample, involving a shift to shorter times, as indicated in Fig. 11. Since the shift rate \(\mu\) is reduced at high stresses, the natural aging behaviour at high stress (Type 1) is much less than at low stresses, as shown by the dashed line in Fig. 11. When repeated high stress creep measurements (Type 2) are made, though, there is an apparently faster aging rate, which may be interpreted as mechanical enhancement.
The above explanation is not universally accepted. It should be pointed out, though, that a conclusion reached by Ngai and Yee in apparent agreement with the mechanical enhancement proposal of Sternstein et al. can be misleading. These authors re-analyse the data of Cama and find the results consistent with the idea that mechanical stress and physical aging have similar effects on the structural state of the glass. This, however, is really only a reformulation of Sternstein's proposal of mechanical enhancement in terms of Ngai's coupling model, in which they find that the coupling constant $n$ increases with successive strain cycles. Strangely, this appears rather at odds with an earlier report on non-linear effects in PC, where the conclusion was reached that non-linear strains dramatically reduce the value of the coupling constant.

It would be fair to say, therefore, that the situation regarding physical aging and high strains or stresses is far from resolved. Indeed, the question of rejuvenation or otherwise continues to be debated today. Support for Struik's idea of rejuvenation under high stresses comes from the torsional dilatometric experiments of Pixa et al. and from an extended investigation by Smith and co-workers. This latter group utilise a kind of “tickle” technique similar to that used earlier by Yee et al., a static strain in the non-linear region (typically in the range 1–6%) is applied, upon which is superimposed periodically a sinusoidal strain of small amplitude, typically less than 0.1%, over a range of frequencies. Some typical results for polycarbonate are reproduced in Fig. 12. These data can be superposed by horizontal shifting to form a master curve, and the shift factor determined in the usual way is found to be significantly greater than unity and to increase strongly with temperature in the range 30–100°C. The usefulness of the shift factor determined in this way is questionable, though, as the data cover only a limited frequency range (less than two decades) and, as can be seen in Fig. 12, appear as rather straight and parallel lines. Thus, vertical shifting will significantly affect the value of $\mu$ found in this way; indeed, vertical shifting alone gives an equally acceptable master curve, and has been used to define an alternative measure of aging rate.
Fig. 12. Frequency dependence of $E'$, the small strain (<0.1%) differential storage modulus, as a function of aging time (here designated by $t_c$ and measured in seconds) for PC subjected to a static tensile strain of 2.6% at 50°C after cooling from above $T_g$. $E_0'$ is the storage modulus determined for zero static strain (reproduced from ref. 202, with permission).

Similar results are obtained by these workers for both tensile and compressive static strains, and the conclusion reached is that the polymer glass is rejuvenated by deformation in either tension or compression. The same conclusion was made by Struik16 who suggested that free volume is created by the deformation process, regardless of whether it is in tension or compression, and proportional to the rate of dissipation of mechanical energy. However, it is not clear to the present reviewer that Smith and co-workers have properly considered the complex interaction of the non-linearity, stress relaxation, and possible rejuvenation, and similar doubts have also been expressed by McKenna and Zapas.203,204 Indeed, McKenna and co-workers argue that the volume recovery, which is considered to be responsible for the universally observed physical aging at low strains, has much less effect on the non-linear mechanical response. More particularly, they find that “large mechanical stimuli do not alter the underlying thermodynamic state of the glass, and aging is not ‘erased’ by large stresses or deformations”. The basis for this dramatically contrasting opinion is summarised below.

A study of physical aging by means of small strain (0.25%) stress relaxation experiments on epoxy networks showed205 that superposition could be effected by horizontal plus slight vertical shifting. The shift factor $\mu$ was in the range 0.80–0.90, in fact increasing with increasing crosslink density. When aged at temperatures sufficiently close to their respective $T_g$'s, these epoxies were seen to age into equilibrium, as evidenced by a more or less abrupt change in slope $\mu$ of the double logarithmic plot from nearly unity to approximately zero at a time denoted by $t^*$, as shown in Fig. 13. The time $t^*$ provides a measure of the “equilibration time”.

When higher strains were applied in these stress relaxation experiments, two effects were observed. First, in agreement with Struik,16 the shift rate $\mu$ decreased; and second, the time $t^*$ remained constant.206 The same observations have also been made in creep.207 It is argued that this latter effect is inconsistent with a rejuvenation
Fig. 13. Double logarithmic plot of shift factor \( a \) (here subscripted \( t_e \)) vs aging time \( t_e \) for epoxy network samples in low strain (0.25%) stress relaxation following a quench from above \( T_g (= 72.3^\circ C) \) to the temperatures indicated: ●, 66.0°C; ○, 62.0°C; □, 57.2°C; △, 51.5°C; ×, 48.3°C; ○, 42.2°C. The times \( t^* \) are determined by the intersections of the lines shown (reproduced from ref. 205, with permission).

process since it would then be expected that, under higher strain, the glass would take longer to reach equilibrium. It is worth noting a couple of points here before proceeding to the next stage in their argument. The time \( t^* \) is defined as the intersection (see Fig. 13) of two straight lines, the longer time branch supposedly representing an equilibrium state. The details of this picture differ significantly, however, from volume and enthalpy relaxation measurements, where there is not an abrupt transition from aging state to equilibrium. Furthermore, in equilibrium, the values of volume and enthalpy remain constant whereas it is a recurring feature of the data of McKenna and co-workers that the shift factor continues to increase with aging time, albeit with only a very shallow slope. It may be that this representation, shown in Fig. 13, of the data as two straight lines conceals a more gradual approach to equilibrium so that the reported values of \( t^* \) do not in fact represent "equilibration times". Support for this view may be gained by estimating the change in \( t^* \) as a function of aging temperature. For example, in Fig. 2 of ref. 206 for an epoxy glass we find \( t^* \) increases by about 0.6 decades for a reduction in aging temperature of 4.0°C. This equates to approximately 6.7°C per decade of timescale, at least a factor of 2 greater than the value usually obtained for polymer glasses.34

The argument of McKenna and co-workers proceeds with the difficult experimental measurement of volume changes during torsional deformation,208 again for epoxy glasses. Following a quench from above to below \( T_g \), they showed again that while the shift rate \( \mu \) decreased with increasing level of strain (1%, 3%, 5%) in stress relaxation, the "equilibration time" \( t^* \) remained constant. Additionally, though, they measured the volume recovery following this quench, and during the aging
process applied torsional strains of one tenth duration of the aging time and of various magnitudes, as before. Their remarkable observation was that, while increasing the torsional strain caused increasingly large instantaneous departures (increases) from the background volume relaxation behaviour, the volumetric recovery always returned to this background without any rejuvenating (or indeed enhancement) effect. Thus equilibrium was attained, for example, in their epoxy at about 9°C below $T_g$ in approximately $10^6$ seconds (a typical equilibration time for polymer glasses at such an undercooling below $T_g$), irrespective of the magnitude of torsional pulses (mechanical stimuli) applied during the recovery.

The conclusion reached from these experiments is that the underlying thermodynamic state of the glass is unaffected by large mechanical stimuli and that volume recovery affects the viscoelastic response more at small strains than it does at large strains. We are clearly some way away from a reconciliation of the various reported effects of high stresses/strains on the aging behaviour, but the simultaneous measurement of viscoelastic response and volume recovery is likely to be a powerful technique for studying such effects. For example, a number of different timescales have been identified approximately: mechanical torque relaxation, recovery of mechanically induced volume changes, recovery of thermally induced volume changes, and the evolution of the mechanically induced volume recovery. The relative magnitudes of these timescales is likely to provide important clues as to the molecular mechanisms, and the interaction of applied stress, volume recovery, and the physical aging process.

5.5. Aging in Semi-Crystalline Polymers

Physical aging has been observed in a very broad range of polymeric materials, including both thermoplastic and thermoset matrix composites and liquid crystalline polymers. These particular polymer materials are not specifically discussed in this review; rather, we examine the aging in semi-crystalline polymers, for which a number of interesting effects have been observed.

One of the earliest reports of the effects of physical aging on the properties of semi-crystalline polymers was the study by Schael of polypropylene (PP) films. He found an increase in modulus and a decrease in impact strength and static coefficient of friction correlated with an increase in density with increasing aging time at temperatures above room temperature. Changes in both crystalline structure and degree of crystallinity must always be considered a possibility in semi-crystalline polymers; this was discussed by Schael, but changes in the amorphous content were also considered, in terms of a reduction in "void" concentration, which may be interpreted as free volume.

The interesting aspect of these results is that the physical aging process is occurring at temperatures above the glass transition temperature of PP, where one might expect the amorphous phase to be in equilibrium. This is not peculiar to PP; the same effect has been reported in a wide range of semi-crystalline polymers (e.g. see ref. 16). Indeed, the aging of semi-crystalline polymers, as measured for example by the creep compliance, is found to be remarkably similar to the aging of amorphous polymers.
This observation led Struik to explain these results in terms of an "extended glass transition" in semi-crystalline polymers.\textsuperscript{16,215}

According to this idea, aging occurs, as in amorphous polymers, as a result of structural changes in the amorphous phase of semi-crystalline polymers. The amorphous phase, however, may be regarded, in a simplified way, as consisting of two regions: the bulk amorphous regions, which are relatively distant from the crystalline lamellae, and constrained amorphous regions, which are close to the surfaces of the crystalline lamellae, and are constrained in their structural rearrangement by these lamellae. This distinction is necessary because the amorphous phase of semi-crystalline polymers is located in the interlamellar region of the spherulites, and will therefore not be able to relax in an unconstrained way like bulk amorphous polymers. It is argued that the constrained amorphous regions will have a higher $T_g$ than the unconstrained regions, the latter having a $T_g$ equal to that of bulk amorphous material. Because of this, there will be a range of glass transition temperatures extending above the $T_g$ of the bulk amorphous material. Hence, one might anticipate physical aging at temperatures above the conventional $T_g$ as structural re-arrangements, and reduction in free volume, occur in these constrained amorphous regions.

This idea was further developed by Struik in an extensive study of physical aging in semi-crystalline polymers.\textsuperscript{216-219} By considering that the effect of the constraints discussed above is to create an "upper" glass transition temperature $T_g^U$, some degrees higher than the conventional glass transition temperature, designated a "lower" glass transition temperature, $T_g^L$, he identifies four different regions of behaviour for the aging of semi-crystalline polymers.

(i) $T < T_g^L$: Both bulk and constrained amorphous regions are below their respective $T_g$'s, and hence typical glassy behaviour of fully amorphous polymers is observed, with a shift rate $\mu$ close to unity. Creep curves at different aging times will be superposable by means of the usual horizontal plus small vertical (downward) shifts.

(ii) $T \approx T_g^L$: In this narrow temperature interval the shift rate $\mu$ begins to decrease as the bulk amorphous regions are approaching equilibrium. Both horizontal and downward vertical shifts are required for superposition.

(iii) $T_g^T < T < T_g^U$: The bulk amorphous regions have now reached their rubbery plateau. If this plateau is not in fact flat, but the compliance increases with time, then the aging behaviour in this region will involve a horizontal component of the shift from the constrained regions plus a vertical upward shift arising from the bulk amorphous regions.

(iv) $T > T_g^U$: In this temperature region, both bulk and constrained amorphous regions are rubbery, and the aging effects disappear, with the shift rate decreasing rapidly from unity.

Struik finds excellent agreement of the predictions of this model with experimental data for many different semi-crystalline polymers, and covering a wide range of temperatures.

Read et al.\textsuperscript{181,220} however, from the results of studies on semi-crystalline polybutylene terephthalate (PBT), high density polyethylene (HDPE), and PP have
questioned this rather universal model of Struik's. In particular, with reference to the physical aging of PP at 20°C, they found the \( \beta \)-relaxation region (corresponding to \( T^*_\beta \)) to be approaching its rubbery plateau for times greater than about one second, together with a significant reduction in \( \beta \)-relaxation strength with aging. They argue, therefore, that the creep data (at times longer than 1 s) should correspond to region (iii) above, involving an upward vertical shift; however, this is opposite to their observed shifts. In addition, they note a broadening and a reduction in the strength of the \( \alpha \)-relaxation region, which implies that superposition by a combination of vertical and horizontal shifts will not be valid. Chai and McCrum\(^{175,221} \) noted also the effect of aging on the relaxation strength and the lack of superposition of creep data for PP aged at 40°C, though as mentioned above this could be a question of subjective judgement. Read et al.\(^{220} \) conclude that, at least in polypropylene, aging at room temperature is controlled by the \( \alpha \)-relaxation process, and suggest a molecular model for this. Consequently, in their view the aging, at least in this semi-crystalline polymer, cannot be fundamentally related to the same structural relaxation processes as those responsible for aging in fully amorphous polymers. Once again, therefore, there are seen to be significantly differing views on the physical aging mechanism.

### 5.6. Theoretical Aspects and Prediction of Aging

We have seen in an earlier section how the volume (and enthalpy) relaxation behaviour of amorphous polymers can be described rather well by theoretical models. As it is commonly assumed that the aging of the viscoelastic response follows the changes in volume, it should be possible to predict the aging of mechanical properties from these models. This has been attempted, with mixed success.

Consider, for example, the KAHR model.\(^{38} \) The dependence of the volumetric relaxation times on structure (\( \delta \)) is given by eq. 16, which may be written in a convenient shorthand notation as:

\[
\tau_i(T, \delta) = \tau_i a_T a_\delta
\]  

(28)

in which \( a_T \) and \( a_\delta \) are the temperature and structure shift factors, respectively, given by

\[
a_T = \exp[-\theta(T - T_r)]
\]  

(29)

and

\[
a_\delta = \exp[-(1 - x)\theta \delta / \Delta \alpha]
\]  

(30)

Aklonis\(^{222} \) used this model, together with the assumption that the distribution of stress relaxation times is uniformly shifted on aging by the shift factor \( a_\delta \), to predict the aging of the viscoelastic response of polyvinylacetate. Whilst qualitative agreement with typical experimental data was obtained, using parameter values in eq. 30 derived from volume relaxation data, it was noted that the shift factor \( \mu \) was predicted to be rather small (0.65) in comparison with the usual value close to unity.\(^{223} \) In fact, a distribution of volume relaxation times broader than about two decades was found\(^{224} \)
to give a maximum shift rate considerably less than unity. Later work\textsuperscript{225} showed that the predicted shift factor was very sensitive to the specific form for the expression for $a_6$, with a modified WLF expression\textsuperscript{118} giving a much better fit to experimental data than does eq. 30. Greiner\textsuperscript{226} has also found the modified WLF expression to be rather successful. This is a rather surprising result, particularly as it had earlier been shown\textsuperscript{118} that the KAHR model, eq. 30 and the modified WLF equation, together with a number of other expressions for the structural dependence of the relaxation time, are all essentially equivalent within a narrow temperature interval close to $T_g$. When considered alongside the very fundamental but unsupported assumption that the viscoelastic spectrum of relaxation times shifts on aging in exactly the same way as does the volume relaxation time spectrum, this additional observation would suggest that it is likely to be very difficult to obtain a meaningful prediction of viscoelastic behaviour on aging.

Attempts have been made similarly to correlate the shift of the viscoelastic spectrum on aging with the enthalpy relaxation behaviour, but no consensus has been reached. For example, Mijovic and Ho\textsuperscript{227} find a remarkably similar dependence between the enthalpic and viscoelastic aging behaviours for PMMA, poly(styrene-co-acrylonitrile), and their blends, whereas Roe and Millman\textsuperscript{55} observe in PS that on aging close to $T_g$ enthalpy reaches an equilibrium value after about 10 h, while the creep behaviour continues to evolve with further aging time. Also, at room temperature, the enthalpy shows no measurable change until about one year of aging, while the creep response began evolving after only a few hours.

And what about those who have observed that creep or stress relaxation data do not superpose as the aging time increases? This can lead to theoretical approaches in which the usual assumption of thermorheological simplicity is abandoned. For example, the coupling model, which has been applied to many aspects of volume and enthalpy relaxation, has also been applied to model the aging of the creep compliance of PS.\textsuperscript{228} The coupling parameter $n$ is found to increase with aging time, causing a change in the shapes of the creep curves, and this introduces a new source of non-linearity. But is it correct to analyse these data, as they do, without any vertical shift, particularly in the light of Read et al.'s observations,\textsuperscript{180–183,220} that, for a variety of amorphous and semi-crystalline polymers, the strength of the $\beta$-relaxation process is reduced on aging, so that the unrelaxed compliance for the $\alpha$-relaxation process must also reduce on aging? Thus, although the coupling model provides a good fit to the experimental aging data for PS,\textsuperscript{228} with no vertical shifting, it seems unrealistic to expect their results to have real physical significance. Their conclusion that aging increases the strength of the coupling of the relaxation mode with its surroundings should therefore be considered cautiously.

A rather more pragmatic approach to modelling creep behaviour and the effects of aging was adopted by Read et al.\textsuperscript{229} based upon their experimental data covering a wide range of times, including both $\beta$- and $\alpha$-relaxation regions. They write the creep compliance at a given age in terms of the contributions from each of these relaxation regions:

$$J(t) = J_{\alpha} + J_\beta(t) + J_\alpha(t)$$

(31)
where $J_{U\beta}$ is the unrelaxed compliance and $J_\beta(t)$ and $J_\alpha(t)$ are the time-dependent compliances for the $\beta$- and $\alpha$-relaxation regions, respectively.

The modelling of the creep response for PMMA, PC, PVC, PBT, PP and HDPE is sensitive to the overlap of these two relaxation regions, which is particularly marked for PMMA. By means of empirical equations describing each term in eq. 31, with parameters to quantify the timescale, strength and breadth of each relaxation process, they were able not only to fit the short term creep data, but also to use these data to predict the long term behaviour. The dependence on aging time of these parameters was not universal to the polymers studied; for example, for PMMA, PVC, PC and PBT, the width of the $\alpha$-relaxation spectrum remained constant on aging, whereas for PP and HDPE allowance had to be made for a change (broadening) of the spectrum on aging. Similarly, differences are also seen in respect of the relaxation strengths. It appears that a good description of creep and aging behaviour can indeed be obtained for individual polymers, but there is no universal behaviour covering the range of amorphous and semi-crystalline polymers.

5.7. Summary

The extensive work of Struik[16] on a very wide range of polymeric and other materials shows a remarkable universality in respect of the physical aging behaviour as manifest, in particular, by the creep response. It is tempting, therefore, to attribute this aging to a rather fundamental concept, and the most commonly adopted explanation is in terms of changes in free volume. In the simplest situation, following a quench from above to below $T_g$, the reduction in molecular mobility as the free volume reduces implies a lengthening of the viscoelastic timescale, and hence a shift of the creep response to longer times. Such shifting of creep (and stress relaxation) data seems to work rather well in the linear viscoelastic region, even though vertical shifting is occasionally necessary, and suggests that the free volume hypothesis is largely correct. This is undoubtedly the case, despite the fact that it is not difficult to find reported instances of a lack of superposition. A number of explanations for this are possible, including, in particular, the question of subjectivity in any decision about goodness of fit in superposition, and the need (or otherwise) to take into account the changes in the limiting compliances (or moduli) on aging.

The situation becomes both more complex and more controversial in the non-linear viscoelastic region, in which an interaction exists between the testing procedure and the aging process. Early reports of a mechanical enhancement of aging due to high stresses have largely been replaced by the opposite effect, a rejuvenation. The effect of rejuvenation is to reduce the double logarithmic shift rate $\mu$ from its value close to unity in the linear viscoelastic region, with an increasing reduction in $\mu$ as the applied stress increases. General agreement on this point, however, does not extend to some other aspects. In particular, there is one school of thought which, on the basis of results obtained from the difficult experimental technique of combined stress relaxation and dilatometry, rejects the idea of rejuvenation because the time required to reach an equilibrium state does not appear to increase with increasing stress. These observations open up the whole question of timescales for a variety of molecular
relaxation processes, including volume recovery, stress relaxation and aging of the mechanical response. This is likely to be a fruitful area for advancing our understanding of the aging behaviour.

Further complications arise when the aging studies are extended to semi-crystalline polymers. Struik has developed a rather detailed explanation of the behaviour of semi-crystalline polymers in terms of an extended glass transition, resulting from the existence of the amorphous phase in essentially two states, a bulk unconstrained state and a constrained state of the amorphous regions close to the crystalline lamellae. This rather neatly explains why it is possible for semi-crystalline polymers to age at temperatures above their supposed glass transition. Once again, however, there are reliable reports of aging behaviours which cannot be explained by this hypothesis, and which raise the question of whether or not the spectrum of relaxation times for a given molecular relaxation process remains constant or changes in shape during aging. Thus we are back again to the issue of thermorheologically simple behaviour, which was seen to be a basic assumption of the majority of theoretical models for physical aging. If this assumption is invalid, then an approach such as that afforded by the coupling model will be required.

6. CONCLUDING REMARKS

The physical aging of polymers has been reviewed here in three broad areas: the changes in bulk thermodynamic properties, namely volume and enthalpy; various microstructural evidence for structural changes; and changes in mechanical properties. It is concluded that there is a remarkably good correlation between these aspects, and that they may broadly be linked through the concepts of free volume and free volume distribution. However, there remain a number of controversial areas where disagreement may arise for a number of reasons. Since these areas frequently include those situations which are of practical or engineering relevance, such as the application of high stresses or the use of semi-crystalline polymers, there is a clear need for these problems to be resolved.

ACKNOWLEDGEMENTS

This review was written whilst on research leave at the Department of Polymeric Materials, Chalmers University of Technology, Gothenburg, Sweden. The permission of Aberdeen University for research leave and the hospitality of Chalmers University are gratefully acknowledged.

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