PHYSICAL REVIEW B VOLUME 39, NUMBER 4 1 FEBRUARY 1989

Molecular theory for the rheology of glasses and polymers

J. Y. Cavaille* and J. Perez
Groupe d'Etudes des Metallurgie Physique et de Physique des Materiaux, Institut National des Sciences Appliquees, 69621 Villeurbanne, France

G. P. Johari
Department of Materials Science and Engineering, McMaster University, Hamilton, Ontario, Canada L8S 4L7

(Received 2 June 1988; revised manuscript received 12 September 1988)

A molecular kinetic theory for the rheology of glass is given. According to this theory, the structure of a glass consists of randomly distributed high-energy sites, which correspond to the frozen-in density fluctuations. These sites are termed as defects. The anelastic deformation associated with the β relaxation in a glass is attributed to the availability of a set of configurational states through the faster, uncorrelated rotational-translational motions of molecules within these defects. These involve a broad distribution of potential energy barriers of lower energy. The nonelastic deformation observed after a long period of time ($\gg 10^4$ sec) is associated with the α process and is attributed to the much slower hierarchically constrained motions of the surrounding molecules, which leads to the growth of sheared microdomains within the glassy matrix. The effect of hierarchical constraints within the microstructural regions is essentially as described by Palmer, Stein, Abrahams, and Anderson [Phys. Rev. Lett. **53**, 958 (1984)]. At a low temperature when the duration for the measurements is long, or at high temperatures when the number of defects is high, sheared microdomains nucleated at one site grow and merge into the others which were nucleated at other sites, thus leading to an irrecoverable macroscopic deformation or viscous flow. The theory is extended to amorphous polymers in which further restrictions on the number of available configurational states is placed by the strength and directionality of covalent bonds and by the entanglements and junction points between the polymer chains. The number of molecules forming the defects was calculated from the thermodynamic data at $T > T_g$, but at $T < T_g$ it was assumed to be the same as at T_g. The result of the theory is a relation practically coinciding with the observed time and temperature dependence of the creep and dynamic-mechanical properties of the glassy state of a material.

I. INTRODUCTION

On the application of a mechanical, or electrical, stress, glassy materials exhibit two types of recoverable deformation whose kinetics are both time and temperature dependent. The first type of deformation involves localized atomic, or molecular, motions within a glassy matrix; the second type involves large-scale atomic, or molecular, motions, and, in a molecular glass, ultimately leads to viscous flow or irrecoverable macroscopic deformation. For a given duration of measurement, the magnitude of the latter type increases rapidly with increase in the temperature and reaches large magnitudes as the temperature approaches the softening or the glass-transition range. In the dynamic-mechanical or dielectric measurement, the different types of deformations appear as separate peaks in the relaxation spectra of the corresponding loss tangents. The high-frequency peak is known as β, and the low-frequency peak as an α process. Their separation in the frequency plane decreases with increasing temperature.

It is now known that the occurrence of localized molecular motions or β relaxation observed at temperatures below T_g (temperature at which viscosity, η, is 10^{12} Pa sec), and in some cases also above T_g, is an intrinsic property of atomically or molecularly disordered substances. It is also observed that the characteristics of the rate of the β-relaxation process do not change when a liquid is cooled from a temperature above T_g to far below it, but those of the α-process do change, namely that the temperature dependence of the rate of the α process changes at a temperature near T_g from the Vogel-Fulcher-Tamman type to an Arrhenius type, with an appreciably high activation energy and low preexponential factor.

Theoretical treatments for the occurrence of molecular motions seen both as α and β processes have been difficult, but a number of qualitative ideas have been advanced in terms of the structure of a glass in order to rationalize them. This paper provides a molecular description and formalism for these behaviors by considering that the molecular motions that determine the rheology of glassy materials begin at particular sites, hereafter called "defects", and evolve with time. The observed deformations or relaxation processes are a manifestation of this evolution. It includes some of the formalisms of similar ideas of each of its authors, who have published them before in different contexts, and also modifies the development of those ideas. For clarity, the theory is dealt with in four sections, namely: (i) structure of a glass as a disordered matrix containing low-(and high-) density regions,[1] or islands of mobility,[2] (ii) anelastic deformation resulting from the formation of sheared domains which grow with the time of the applied stress[3]; (iii) the development with time of molecular motions that appear as β and α processes, and viscous flow, their treatment in terms of hierarchically constrained motions, as originally given by Palmer, *et al.*[4] and modified here, and (iv) their formalism in terms of measurable quantities, the shear compliance and modulus. The theory is followed by a discussion of its prediction of time dependence in Sec. V and then the temperature dependence in Sec. VI, of the creep compliance and the dynamic mechanical behavior of both molecular glass and amorphous polymers[5] with chain entanglements and junction points. Several experimentally testable consequences of the theory are given in Sec. VII. Since 1986, when this work was done, some of the ideas given here have been used to develop theories for the calorimetric and aging behaviors of polymers by Perez[6] and for the rheology of polymers near the glass-transition region by Perez, *et al.*[7]

II. STRUCTURE OF A GLASS

In recognition of the central idea that fluctuations of the local fluid structure from point to point within a liquid become frozen-in at the glass-transition temperature, the concept of the heterogeneity of the microscopic structure of a glassy material has been implied in a number of theories. Amongst these are the free volume theory by Cohen and Turnbull,[8] and its extension in terms of "liquidlike" and "solidlike" regions by Cohen and Grest,[9,10] cell model by Robertson, Simha, and Curro,[11] heterogeneous structure model for kinetic behavior by Brawer,[12] and its further description in terms of a "master equation" by Dyre,[13] the configurational entropy theory by Adams and Gibbs,[14] and defect structure by Slorovitz *et al.*[15] and by Cunat.[16] These theories explain the characteristics of liquid and glass relaxations reasonably adequately, although they provide no explanation for the existence of β relaxation in a glass. That such heterogeneity may also be responsible for β relaxations in molecular glasses was suggested by Johari and Goldstein[17] and by Johari[18] in recognition of the fact that the occurrence of a β relaxation is intrinsic to the nature of a glassy material.

Accordingly, the structure of a glass may be considered as a random distribution of local regions of (spatially) fluctuating density and high energy, or entropy, in an atomically or molecularly disordered continuum. In these local regions, a molecule together with its first neighbors forms a group of molecules which remains in an internal thermodynamic equilibrium. Molecules in these groups are capable of undergoing thermally activated Brownian motions at temperatures substantially below T_g—motions that show up as a secondary or β relaxation in the dielectric and mechanical spectroscopy and in the NMR relaxation studies. Let the number of molecules that form the local regions, or defects, be in a concentration n per mole, so that the relative concentration of molecules forming such regions with respect to the total number of molecules, $C_D = n/N_A$, where N_A is the Avogadro number. The presence of such regions would increase the Gibb's free energy of a glass by an amount nG_{exc}, where G_{exc} is the increase in the free energy of an atom or a molecule when taken from the mean density region to the low- or high-density regions in the structure.

Since the concentration of such local regions in the glass is the same as that which freezes in at its T_g, we assume that this concentration remains constant with changing temperature below T_g if spontaneous structural relaxation does not occur. But, for temperatures above T_g, C_D increases according to the Boltzmann distribution

$$C_D = \frac{n}{N_A} = \frac{1}{1+\exp(G_{\text{exc}}/k_B T)} , \quad (1)$$

or

$$C_D = \frac{1}{1+\exp(H_{\text{exc}}/k_B T)\exp(-S_{\text{exc}}/k_B)} , \quad (2)$$

where, $G_{\text{exc}} = H_{\text{exc}}, -TS_{\text{exc}}$ for one molecule. This means that the density fluctuations in a liquid are rapid and an equilibrium value of C_D is attained at each temperature above T_g within the experimental time scale. Equation (2) implies that the vibrational contribution to the thermodynamic properties of the glass and its corresponding crystalline state are the same, i.e, in the absence of such regions the thermodynamic properties of a glass and a crystal are identical.

At a temperature above T_g, a continuous, thermally activated, redistribution of molecules in such defects occurs and this is tantamount to the availability of a number of configurational states over a time scale, τ, of less than 10^4 sec (T_g is defined here as the temperature at which molecular motions freeze out on an experimental time scale of 10^3 sec according to $\eta = G\tau$, where $G \approx 10^9$ Pa).[5] Upon sufficient fluctuations in energy or enthalpy, the molecules within the defects can rearrange into another configuration independently of their environment.

In their theory for cooperative motions in liquids near T_g, Adams and Gibbs[14] showed that the average transition probability into another configuration at a temperature T is given by

$$\overline{W}(T) \propto \exp(-z^*\Delta\mu/k_B T) , \quad (3)$$

where z^* is the number of molecules undergoing a cooperative motion. By assuming that the configurational entropy is uniformly distributed among all molecules, they calculated that

$$z^* = N_A(S_c^*/S_c) , \quad (4)$$

which led to

$$\overline{W}(T) \propto \exp\left[-\frac{N_A S_c^* \Delta\mu}{S_c k_B T}\right] , \quad (5)$$

where S_c^* is the critical configurational entropy, $\Delta\mu$ is the excess chemical potential, and S_c is the configurational entropy.

Alternatively, we suggest that the configurational entropy is distributed only amongst the molecules in the defect sites, so that $S_c = nS_{\text{exc}}$. Therefore,

$$\overline{W}(T) \propto \exp\left[-\frac{N_A S_c^* \Delta\mu}{n S_{\text{exc}} k_B T}\right], \tag{6}$$

or

$$\overline{W}(T) \propto \exp\left[-\frac{B}{C_D k_B T}\right], \tag{7}$$

where $B = \Delta\mu S_c^* / S_{\text{exc}}$, a quantity independent of temperature and $n = C_D N_A$. Thus, in Eq (7), C_D, instead of S_c, becomes the order parameter. It is noteworthy that in our formalism, the domains of cooperative movements are limited to the defect, i.e., a molecule which forms with its first neighbors a high-energy site.

The mean time for a transition, $\tau(T)$, is related to the inverse of the probability, $\overline{W}(T)$ in Eq. (7). Therefore,

$$\tau(T) = \frac{h}{k_B T} \exp\left[\frac{B}{C_D k_B T}\right], \tag{8}$$

where h is Planck's constant, and B is a constant with dimensions of energy. According to Eq. (8), τ explicitly depends on the concentration of defects, C_D, at a temperature T.

The translational-rotational diffusion coefficient, D, of a molecule is given by,

$$D = \nu_0 \lambda^2 \exp\left[\frac{B}{C_D k_B T}\right], \tag{9}$$

where $\nu_0 = (k_B T / h)$, and λ is the mean distance of displacement of a molecule at $T \geq T_g$.

We suggest that the relative concentration of molecules forming defect sites or C_D, can be calculated from the difference between the enthalpy of the liquid and the crystalline solid from Eq (2) as follows: If ΔC_p is the difference between the measured heat capacity of the liquid and the crystal at a temperature T near T_g, then

$$N_A C_D H_{\text{exc}} = \Delta H \simeq \Delta C_p (T - T_2), \tag{10}$$

where T_2 is the extrapolated temperature at which, according to the Adams and Gibbs theory,[14] the linearly extrapolated enthalpy of the supercooled equilibrium liquid at $T < T_g$ would become equal to that of the crystal. Measurements[14] on most molecular liquids and polymers have shown that $1.2 \leq (T_g / T_2) \leq 1.5$. Therefore, from Eq. (10)

$$C_D(T_g) = \frac{\Delta C_p T_g (1 - T_2 / T_g)}{H_{\text{exc}} N_A}, \tag{11}$$

and at T near T_g,

$$(\partial C_D / \partial T) = (\Delta C_p / H_{\text{exc}} N_A). \tag{12}$$

Since H_{exc}, the difference between the enthalpy of a molecule forming the defect and of the molecule that is outside the defect, is expected to remain constant with changing temperature, C_D increases linearly with $\Delta H(T)$ with an approximate slope of $\Delta C_p / H_{\text{exc}}$. The detailed arguments in its support have been given earlier by one of us.[1] H_{exc} and S_{exc} can be calculated from Eqs. (2) and (10) with their derivatives, $(\partial C_D / \partial T)$ at T_g, and therefore C_D can be estimated. We use these estimates in Sec. V.

III. NONELASTIC DEFORMATION OF A GLASS NEAR T_g

In an earlier paper[1] we had proposed that the deformation mechanism at an atomic level in a liquid above T_g involves the transfer of an applied stress, through mainly an elastic medium, to those regions in the bulk of the substance which are soft, i.e., where resistance to shear is significantly weaker than in the rest of the material. The molecules in these regions, or defects, are in a state of high energy, and entropy, and have a volume different from those in other regions which are closely packed. The thermally activated Brownian movement of a molecule or a group of molecules in these regions, or "soft sites," is first to become biased by an applied stress. We envisage that at such sites the shear microdomains are nucleated or begin to form. Thus, the nucleation of shear microdomains begins at those "soft" regions where molecules are in an internal thermodynamic equilibrium. These initial or primary motions, in our theory, correspond to the sub-T_g or the β relaxations. A detailed description of the growth of such shear microdomains has been given by one of us earlier,[19] but it is useful to describe again the general concepts of such domains here. In a shear microdomain, the shear is along a surface S and molecular rearrangements occur inside the volume of such domains which is limited by a surface Σ. The intersection of the two surfaces, namely of Σ and S defines a curve C_n, which separates or distinguishes between the area where shear has occurred from the area where shear has not occurred. According to the mechanics of continuous media as discussed in Ref. 19, the line C_n is a dislocation loop. But in amorphous solids, such dislocations are of Somigliana type and, therefore, line C_n, being a Somigliana dislocation, acts as a sessile or immobile defect. The net effect of this is that the shear remains confined within the microdomain. If the applied stress is maintained for a relatively long time, the stress biased diffusion of molecules between the microdomains occurs and this causes the size of the shear microdomains to increase. On the removal of the applied stress, the domain recovers its initial configuration in a time τ_f as a result of the elastic energy of the line C_n and the thermally activated Brownian motions. Thus the system retains its memory. This means that in this regime of deformation, hereafter called "nonelastic regime," the number of defects and their distribution remains unchanged, and if the stress is removed the defects *are recovered* at their original sites. The duration of this recovery is the same as required during the shearing of a microdomain and its subsequent, diffusion-assisted, recoverable growth. This corresponds to the anelastic behavior observed near T_g.

After a relatively long period of the applied stress, when the growth of a microdomain has occurred up to a certain distance and when similar lines originating from neighboring defect sites merge, the line C_n loses its elastic energy, or identity. This leads to a viscous flow. In order to be consistent with the experimental observations, it is necessary to assume that after the annihilation of shear microdomains, the previous defect sites continue to act as shear sources. A justification for this was discussed in Ref. 19, which considered that these are also a cause of singularity of stress which results in a behavior similar to the Franks and Read's sources of dislocation jogs in crystals. Consequently, the mechanism for the deformation given here need not imply a change in the number of defects, even though their configuration and/or distribution become altered.

A quantitative description of the preceding mechanism for the deformation of a glassy solid leads to an equation,[19]

$$\frac{dn(t)}{dt}=-\frac{n(t)-n(\infty)}{\tau_f}+\frac{n(o)-n(t)}{\tau_D}, \tag{13}$$

where $n(t)$ is the number of defects which remain unactivated at time t and do not produce a shear microdomain, $n(o)$ is the total number of defects at $t=0$, and $n(\infty)$ is the number of defects that remain unactivated on the application of a stress. τ_f is the characteristic time corresponding to defect activation required for inducing a shear microdomain and its subsequent growth, and τ_D is the characteristic time corresponding to the diffusion-assisted annihilation of neighboring lines. Thus, the first term on the right-hand side of Eq. (13) is the rate of both nucleation and growth of shear microdomains, and the second term is the rate of annihilation of dislocation lines C_n, which borders the growing microdomain.

On integration, Eq. (13) gives the shear compliance J at time t, during the growth of shear microdomains

$$J(t)=\frac{\dot{\gamma}}{\sigma}=A\left\{\frac{\tau_D(\tau_D-\tau_f)}{(\tau_f+\tau_D)^2}\left[1-\exp\left[-\frac{t}{\tau}\right]\right]+\frac{2t}{\tau_f+\tau_D}\right\}, \tag{14}$$

where $1/\tau=1/\tau_f+1/\tau_D$ and

$$A=\alpha\Delta\gamma f V_a V_l N_0/k_B T\ .$$

$\alpha\approx 0.1$ is a constant, $\Delta\gamma$ is the elemental shear, f, the Schmid factor, V_a, the activation volume for the formation of a shear microdomain, V_l, the volume per molecule in the shear microdomain, and N_0 is the number of defects per unit volume, i.e., $C_D=N_0V_l$. Schmid factor is a geometrical term which converts the normal stress to its shear component within the shearing surface. Its value is in the range 0.3–0.5.

IV. TYPES OF MOLECULAR MOTIONS

A. General equations

On the application of a stress, glassy materials show usually two types of anelastic behavior, one at short times and lower in amplitude, known as β relaxation, and the other at long times known as α relaxation and nearly ten times greater in magnitude. The rate of the β process follows an Arrhenius behavior with an activation energy of $\sim$40–80 kJ/mol, but that of the α process follows the Vogel-Fulcher-Tamman equation. But, at temperatures below T_g, i.e., in the isoconfigurational state, the rate of the α process follows an Arrhenius behavior with an apparent activation energy of 200–400 kJ mol.[19] The temperature dependence of the α relaxation at $T>T_g$ is attributed to the cooperative character of molecular motions and the term "cooperativity" is used to mean concerted or simultaneous motions of atoms or molecules within a given volume. The broad spectrum of times for the α process is usually regarded as a result of many processes acting in parallel with, and independently of, each other, with a characteristic time τ_i, which in turn is spread over a range of times from zero to a maximum value. These processes may also be expressed in terms of a stretched exponential, or Kohlrausch,[20] or Williams-Watt's[21] equation, $\exp[-(t/\tau)^\beta]$, where $0<\beta<1$.

A number of mathematical models have been recently developed to represent the nonexponential or stretched exponential decay function. These consider a variety of descriptions as, for example, correlated states by Ngai and White[22] and Dissado and Hill,[23] by Ngai *et al.*[24] and Ngai and Rendall,[25] by Bendler and Schlesinger,[26] hierarchical constraints by Palmer *et al.*,[4] fractal and percolation structures by Rammal,[27] fractal free-energy model by Dotsenko,[28] and fractal time model by Hong *et al.*[29] It is conceivable that any of these models could be adapted for use in our molecular theory, but we found Palmer *et al.*'s formalism[4] more suitable for the microstructural processes. In this model the arrangement of relaxation processes is in series rather than parallel, and this is equivalent to a hierarchy of degrees of freedom, from fast to slow, which is now expressed in terms of correlations. In our theory here, the fastest motion corresponds to the single-molecule motion resulting in the activation of a defect as described previously and other molecules or groups of molecules, might only be able to significantly move when several of the fastest moving molecules happen to be placed in just the right way. This requirement is equivalent to the weakening of the intermolecular forces when the distance between molecules increases as a result of the primary but faster motion. Accordingly, the change in the atomic configurations within a domain would involve a series of stepwise motions, each subsequent motion possible by the occurrence of the preceding one. In our consideration, this means that the applied stress initially biases the motion of the molecules within the defect or "soft" sites in the matrix of a glass and the subsequent motions of the surrounding molecules produce a shear microdomain.

We use Palmer *et al.*'s[4] treatment of such motions in terms of the spin levels and the available degrees of freedom. Therefore, we consider that a spin represents a double potential energy well, and the degrees of freedom represent the number of molecules able to move in a particular level of that well. Accordingly, each spin in level

$n+1$ is only free to change its state if a condition of other spins in level n is satisfied. The condition is that the number of spins in level n, i.e., μ_n attains one particular state of their 2^{μ_n} possible states. $\mu_n \le N_n$, where N_n is the total number of degrees of freedom, or molecules, in level n. This gives

$$\tau_{n+1}=2^{\mu_n}\tau_n \tag{15}$$

or

$$\tau_{n+1}=\tau_1 \exp\left[\sum_{1}^{n} \ln 2(\mu_n)\right] . \tag{16}$$

In order to keep τ_n finite as n increases, Palmer *et al.*[4] postulated that the number of spins in level n is determined by a power law,

$$\ln 2(\mu_n)=\mu_0 n^{-p} , \tag{17}$$

where $p=1+\epsilon$, and $0<\epsilon \ll 1$. Alternatively, we suggest that a constant value of time, t_1, is required for the system to move from level n to level $n+1$. This means that for the system to move from level 1 to level n, the time required is $t_n=nt_1$. Thus, n in Eq. (17) may be replaced by (t_n/t_1), and

$$\ln 2(\mu_n)=\mu_0\left[\frac{t_n}{t_1}\right]^{-p} . \tag{18}$$

This introduction of the time required for the change between the levels makes the Palmer *et al.* formalism[4] applicable to the microstructural processes, as it now implies that a change in the level of the system is equivalent to a time-dependent molecular movement. Therefore, instead of Eq. (17), we use Eq. (18) and by substituting it in Eq. (16), we obtain

$$\tau(t)=\tau_1 \exp\left[\mu_0 \sum_{1}^{n}\left[\frac{t_n}{t_1}\right]^{-p}\right] . \tag{19}$$

We consider that the total number of levels is high so that the change in energy between the levels is almost continuous, and the sum in Eq. (19) may be represented by an integral

$$\tau(t)=\tau_1 \exp\left[\mu_0 \int_1^n \left[\frac{t}{t_1}\right]^{-p} d\left[\frac{t}{t_1}\right]\right] , \tag{20}$$

and therefore,

$$\tau(t)=\tau_1 \exp\left[\mu_0\left[\frac{(1-n^{1-p})}{(p-1)}\right]\right] . \tag{21}$$

Thus, when μ_0 in Eq. (19) is zero, $\tau(t)=\tau_1$, the effect due to correlations are minimum, and when $\mu_0=1$, the effects due to correlations are maximum. Accordingly, the relaxation time is an increasing function of time, and the higher the value of μ_0, the greater is the dependence of τ upon t. These equations thus form a generalized condition for molecular motions, which we now use for a description of the β and α processes.

B. The β-relaxation process

As proposed in Secs. II and III, each loosely-packed defect molecule in the glassy matrix can undergo a hindered rotational-translational motion.[2,18] Thus, for each molecule in the defect, $N_0=1$, i.e., that the system has only one degree of freedom. At such sites of hindered molecular motions, correlation effects arising from hierarchical constraints can be ignored since the experimental time is less than τ_1. Each molecule involved in such a motion has only two possible states of energy and no further conditions need to be satisfied for the occurrence of a transition.

The relaxation time, $\tau(t)$ of the molecules forming the defects is not constrained by the hierarchy of the dynamics at the time scale of β relaxation, and is given by

$$\tau(t)=\tau_1=\tau_0 \exp\left[\frac{U}{k_B T}\right] . \tag{22}$$

The resulting relaxation process may be identified as a β- or sub-T_g relaxation process. Because the environment or local arrangement of molecules forming the defect varies as a result of the molecular disorder, U is distributed over a certain range, in the most simple consideration, according to a Gaussian function

$$\tau_{1,i}=\tau_0 \exp\left[\frac{U_i}{k_B T}\right] , \tag{23}$$

with $U_i=U$. Thus the shear compliance due to the β process at time t is

$$J_\beta(t)=A_\beta\left\{\sum_i\left[1-\exp\left[-\frac{t}{\tau_{1,i}}\right]\right]g_i\right\}\Big/\sum_i g_i , \tag{24}$$

and its Fourier transform,

$$J_\beta^*(i\omega)=A_\beta\left[\sum_i\left[\frac{1}{1+i\omega\tau_{1,i}}\right]g_i\right]\Big/\sum_i g_i \tag{25}$$

and

$$g_i=\exp[-(U-U_i)^2/2(\Delta U)^2] , \tag{26}$$

where ΔU is the width of the Gaussian distribution. Thus

$$J'_\beta(\omega)=A_\beta\left[\sum_i \frac{g_i}{1+\omega^2\tau_{1,i}^2}\right]\Big/\sum_i g_i \tag{27}$$

and

$$J''_\beta(\omega)=A_\beta\left[\sum_i \frac{g_i\omega\tau_{1,i}}{1+\omega^2\tau_{1,i}^2}\right]\Big/\sum_i g_i , \tag{28}$$

where (A_β) is defined in Eq. (14), except that here the value of the activation volume V_a and the elemental shear $\Delta\gamma$ correspond only to the activation of defects.

C. The α relaxation

For the condition, $0<\mu_0\le 1$, the requirement for correlated movements of the molecules is more severe, or that the effects of hierarchical constraint are important and $\tau(t)$ can reach the maximum value, $\tau_{\max}$. Thus, the relaxation time at any value of t is greater than τ_1, the relaxation time for the β process.

As mentioned earlier here, Palmer *et al.*[4] suggested that the value of p in Eq. (17) must be greater than, but close to, unity in order to keep $\tau(t)$ from reaching an infinite value. Since p cannot be *a priori* determined for our purposes, we keep $p=1$ and choose a functional form of $\tau(t)$ against t, according to which $\tau(t)$ reaches a maximum value, $\tau_{\max}$, at a cutoff time and beyond this $\tau(t)$ remains constant with t, i.e., $\tau(t)=\tau_{\max}$, if $t \geq \tau_{\max}$, that is that $\tau(t)$, instead of reaching an asymptotic limit, reaches its limit in a finite time. This choice serves the same purpose in limiting the increase in $\tau(t)$ with t, as did Palmer *et al.*'s[4] choice of $p>1$.

Expanding Eq (21) as a series with $\rho \sim 1$ and retaining only the first term to $\tau_{\max}$

$$\tau(t)=\tau_1\left[\frac{t}{t_1}\right]^{\mu_0}+\cdots , \tag{29}$$

when $\tau(t=\tau_{\max})=\tau_{\max}$,

$$\tau_{\max}=(\tau_1 t_1^{-\mu_0})^{1/(1-\mu_0)} , \tag{30}$$

$$\tau(t)=\tau_{\max}^{1-\mu_0} t^{\mu_0} . \tag{30a}$$

Substituting Eq. (30a) in Eq. (23) and replacing $(1-\mu_0)$ by κ, we obtain

$$\tau_{\max}=\tau_0^{1/\kappa} t_1^{(\kappa-1/\kappa)} \exp\left[\frac{U}{\kappa k_B T}\right] . \tag{31}$$

This equation satisfies the condition that for $\tau_1 < t < \tau_{\max}$

$$\tau(t)=\tau_{\max}^{\kappa} t^{1-\kappa} , \tag{32}$$

and for $t \geq \tau_{\max}$, $\tau(t)=\tau_{\max}$.

Thus the hierarchical constraints cause the time dependence of the shear deformation of microdomains (as a result of thermally-activated Brownian motions) to acquire the form of a Kohlrausch function.[20] (This development is different from those given by others,[25–29] which provides a mathematical model for the Kohlrausch function.) The time represented by τ_f in Eq. (13) corresponds to the α process and is governed by the first term on the right-hand side of Eq. (13), and

$$\tau_{f,\max}=(\tau_1 t_1^{\kappa-1})^{1/\kappa} , \tag{33}$$

$$\tau_f(t)=\tau_{f,\max}^{\kappa} t^{1-\kappa} , \tag{33a}$$

where κ, as defined earlier, is less than unity.

The second term in Eq. (13) is related to the rotational-translational diffusion of molecules with a time τ_D, and corresponds to the viscous flow. The time dependent values of shear compliance due to the anelastic process, $J_{\text{anel}}(t)$, and the viscous flow, $J_v(t)$, are then given by

$$J_{\text{anel}}(t)=A\left\{1-\exp\left[-\frac{1}{\kappa}\left[\frac{t}{\tau_{f,\max}}\right]^{\kappa}\right]\right\} \tag{34}$$

and

$$J_v(t)=\frac{At}{\tau_D} . \tag{35}$$

The shear compliance in the α-process $J_\alpha(t)$, is the sum of the anelastic and viscous compliances,

$$J_\alpha(t)=J_{\text{anel}}(t)+J_\beta(t) . \tag{35a}$$

The growth of a shear microdomain would terminate, when $\tau_{f,\max}=\tau_D$, then for $t>\tau_{\max}, J_v(t)>J_{\text{anel}}(t)$, and keeping only the first term of the series of $J_{\text{anel}}(t)$ of Eq. (35)

$$J_\alpha(t)\simeq A\left[\frac{1}{\kappa}\left[\frac{t}{t_{\max}}\right]^{\kappa}+\frac{t}{\tau_{\max}}\right] . \tag{36}$$

The Fourier transform of Eq. (36) gives

$$J_\alpha^*(i\omega)\simeq A\left[\frac{\Gamma(\kappa+1)}{\kappa}(i\omega\tau_{\max})^{-\kappa}+(i\omega\tau_{\max})^{-1}\right] , \tag{37}$$

where $\Gamma(\kappa+1)$ is a gamma function, and $1<\kappa+1<2$. Therefore, $0.88<\Gamma(\kappa+1)<1$, and we assume that $\Gamma(\kappa+1)\simeq 1$.

Thus,

$$J_\alpha^*(i\omega)\simeq A\left[\frac{(i\omega\tau_{\max})^{-\kappa}}{\kappa}+(i\omega\tau_{\max})^{-1}\right] , \tag{38}$$

$$J'_\alpha(\omega)=\frac{1}{G_u}\left[\frac{1+y\cos(\kappa\pi/2)}{[1+y\cos(\kappa\pi/2)]^2+[y\sin(\kappa\pi/2)+(\omega\tau_{\max})^{-1}]^2}\right] , \tag{39}$$

$$J''_\alpha(\omega=\frac{1}{G_u}\left[\frac{y\sin(\kappa\pi/2)+(\omega\tau_{\max})^{-1}}{[1+y\cos(\kappa\pi/2)]^2+[y\sin(\kappa\pi/2)+(\omega\tau_{\max})^{-1}]^2}\right] , \tag{40}$$

where

$$y=(\omega\tau_{\max})^{-\kappa}/\kappa . \tag{40a}$$

V. THE TIME-DEPENDENT DYNAMIC-MECHANICAL BEHAVIOR

A. Molecular glasses and low-molecular weight polymers

The complete equation for the dynamic compliance now involves four terms: (i) the unrelaxed or high-frequency compliances, i.e., G_u^{-1} at $t=0$, (ii) the compliance due to the β process which involves the preliminary step of uncorrelated molecular motions within the defects, (iii) compliance due to the α process as a result of correlated motions within hierarchical constraints of the molecules within a shear microdomain which cause it to become sheared, and (iv) the compliance due to correlated motions of molecules involved in the diffusion process that cause the lines bordering the shear microdomains to lose their identity. We write,

$$J(t)=\frac{1}{G_u}+J_\beta(t)+J_{\text{anel}}(t)+J_v(t)\ . \qquad (41)$$

Theoretically calculated curves for $J(t)$ and $G(t)$ are shown as a function of time in Fig. 1, and G' and G'' are shown as a function of frequency in Fig. 2(a). In Fig. 2(b), the mechanical loss tangent is also plotted as a function of frequency. These curves show the three regions of rheology, namely, the β process, the anelastic process, and the viscous flow, each of which is observed in glassy materials. The value of the various parameters are: $A=3\times10^{-10}$ Pa^{-1}, $A_\beta=1\times10^{-10}$ Pa^{-1}, $U=60$ kJ mol^{-1}, $\Delta U=5$ kJ mol^{-1}, $\kappa=0.30$, $\tau_{\max}=6$ sec, and $T=355$ K.

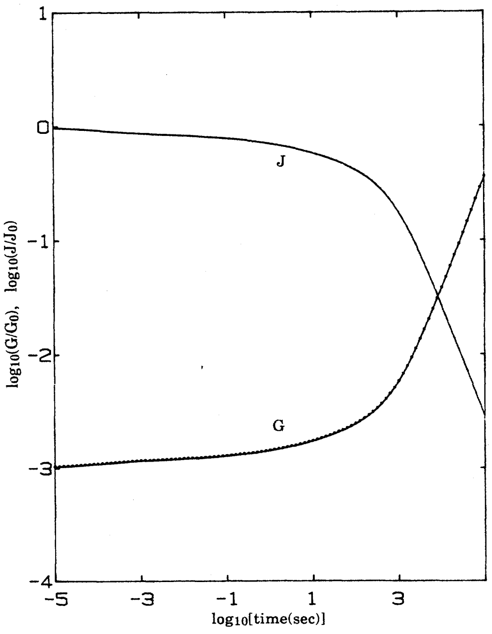

FIG. 1. The theoretically calculated values of shear modulus G and shear compliance J plotted logarithmically against time (see text for details). G is shown by dots-containing curve and J by the smooth curve.

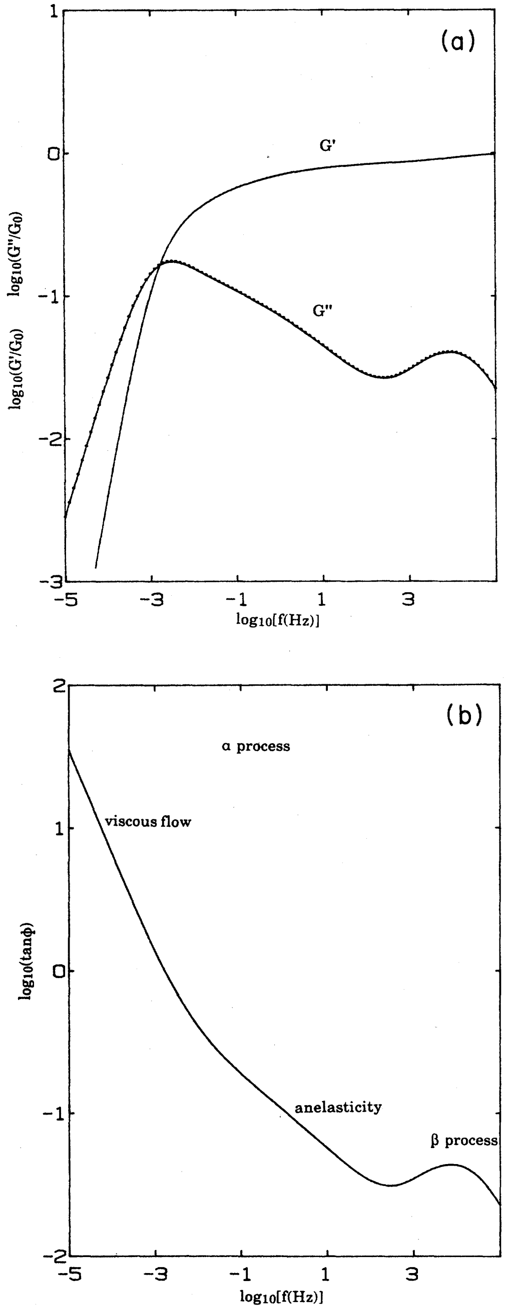

FIG. 2. The theoretically calculated values of: (a) the real and imaginary parts of shear modulus, G' and G'', respectively, and (b) the tanϕ plotted logarithmically against frequency. Parameters used in the calculations are given in the text and are the same as in Fig. 1. G'' is shown by the dots-containing curve and G' by the smooth curve.

B. The entangled and cross-linked polymers

We now consider an extension of Eq. (41) to include both the rubber-elastic and terminal zone behaviors of the entangled, or cross-linked, polymer chains, and when the entanglement effects become low enough to allow the long-range diffusion of a polymer chain. The motion of chain segments is equivalent to the restricted motions of molecules, as mentioned earlier here. For this we use the rubber elasticity theory given by Doi, Edwards and deGennes.[30,31] The rubber modulus G_R relaxes with a time τ_e, which is the time for the disengagement of a polymer chain from its reptation tube according to the Doi-Edwards-deGennes model.[30,31] τ_e is given by, $\tau_e = L^2 \xi_m / \pi^2 q^2 k_B T$, and G at time $t \gg \tau_e$ by

$$G_R(t) = G_R \sum_q \frac{8}{\pi^2 q^2} \exp(-t/\tau_e) . \tag{42}$$

As $t \to \infty$, $G_R(t) \to 0$. Here, L is the length of the tube along which the chain reptates; ξ_m, the molecular friction coefficient, and q is taken as an odd number in the theoretical description. The effect on G due to the rubber modulus can be taken to be in parallel, as illustrated in Fig. 3, with the combined effects of shear microdomain formation and the diffusion that leads to viscous flow.

The diffusion of monomeric segments in an entangled chain or cross-linked polymer is restricted to within the points of entanglements or crosslinks. When the distance between the entanglements is high, the segments can acquire one of the many conformations or configurations, each of which has the same entropy.

In Eq. (41), when $t \ll \tau_\beta$, $J(t) \simeq G_u^{-1}$. But when $t \simeq \tau_\beta$, $J(t) \simeq G_u^{-1} + J_\beta(t)$. Furthermore, when $\tau_\beta \ll t < \tau_{f,\max}$, $J(t) \simeq J_{\text{anel}}(t)$ and for $t > \tau_{f,\max}$, $J(t) \simeq J_v(t)$. Clearly, the use of the parameter κ is made only in the time range of $\tau_\beta \ll t < \tau_{f,\max}$. As was mentioned earlier in Sec. III, the shear microdomains are continually nucleated in the viscous flow region and their growth ultimately leads to the loss of identity of lines that border them. But as long as the strain rate is low and spontaneous structural relaxation or physical aging does not occur, the number of defect sites do not change, and therefore the conditions of correlated movements remain unchanged for molecular or atomic glasses and low-molecular weight polymers.

For high-molecular-weight polymers with entanglements and junction points, the local shear that appears near the defect sites causes a decrease in the degree of freedom of the chain segments as the segments become locally extended. Therefore, as the shear strain increases (or equivalently when the time for the applied stress increases) in the viscous flow region, i.e., when $t > t_{f,\max}$, correlation effects should increase, or in our formalism κ should decrease. As an approximation, we suggest that κ decreases linearly with t, according to

$$\kappa(t) = \kappa \left[1 - a \frac{(t - \tau_{f,\max})}{\tau_{f,\max}} \right] , \tag{42a}$$

where a is an empirical constant, and combine Eq. (42a) and Eq. (33) for the condition that $\tau_D = \tau_{f,\max}$. Thus we obtain (see Appendix I for this derivation)

$$\tau_D(t) \simeq (\tau_{f,\max})^{\chi} t^{1-\chi} , \tag{43}$$

where

$$\chi = 1 - a \ln\left(\frac{\tau_{f,\max}}{t_1}\right) , \tag{43a}$$

and $0 < \chi < 1$, and $0 < \kappa < \chi < 1$.

It follows that $J_{\text{anel}}(t)$ of Eq. (41) is determined by the initial value of κ, as $t \to \tau_{f,\max}$. The correlated motions become more constrained as t further increases and this would cause an increase in $\tau_D(t)$ with time according to Eq. (43). The rate of increase in the constraints which is caused by the local segmental extension as the strain increases is thus determined by the parameter χ.

In physical terms it means that when the distance between the junction points is small, the local percentage extension is large and κ becomes more time dependent, which in turn causes χ to become small. As the distance between the junction points is increased, $\chi \to 1$ and $\tau_D = \tau_{f,\max}$. Thus there is a correlation between the hierarchical constraints and the molecular weight of a polymer. By substituting Eq. (43) in Eq. (35), we obtain for a rubbery polymer

$$J_v(t) = \frac{A}{\chi} \left[\frac{t}{\tau_{D,\max}} \right]^{\chi} . \tag{44}$$

The total compliance $J^*(i\omega)$ at a temperature where viscous flow begins is equal to the sum of $J_\beta^*(i\omega)$, and the compliance due to the α process and viscous flow

$$J^*(i\omega) = J_\beta^*(i\omega) + \frac{1}{G_u} + A \left[\left[\frac{i\omega\tau_{\max}}{\kappa} \right]^{-\kappa} + \left[\frac{i\omega\tau_{\max}}{\chi} \right]^{-\chi} \right] , \tag{45}$$

where $J_\beta^*(i\omega)$ is given by Eq. (24).

The $\tau_{\max}$ of the equations given in Secs. III and IV may now be related to the experimentally observed mechanical relaxation time, τ_m, as defined by the Cole-Davidson function in the form given by Ferry (in Ref. 5). This form gives,

$$J^*(i\omega) = J_\beta^*(i\omega) + \frac{1}{G_u} [1 + C(i\omega\tau_m)^{-\chi} + (i\omega\tau_m)^{-\kappa}] , \tag{46}$$

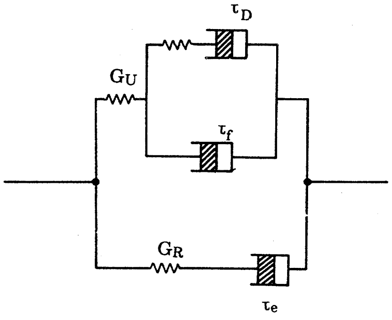

FIG. 3. A schematic representation of the rheological behavior given by the theory including the entropic elasticity or rubber modulus and viscous flow allowed by the chain disentanglements.

where

$$C=(\kappa^{\chi/\kappa}/\chi)(AG_u)^{-(\chi/\kappa-1)} . \tag{47}$$

C is a constant for a material at a given temperature. Thus,

$$\tau_m=\tau_{\max}(AG_u/\kappa)^{(-1/\kappa)} , \tag{48}$$

and the ratio, $(\tau_m/\tau_{\max})$, has a fixed value at a given temperature.

Since $(G_u-G_R)\simeq G_u$, Eq. (45) may be written as

$$G'(\omega)=\frac{J'(\omega)}{J'(\omega)^2+J''(\omega)^2}+G_R'(\omega) , \tag{49}$$

$$G''(\omega)=\frac{J''(\omega)}{J'(\omega)^2+J''(\omega)^2}+G_R''(\omega) , \tag{50}$$

$$J'(\omega)=J_\beta'+\frac{1}{G_u}\left[1+(\omega\tau_m)^{-\kappa}\cos\frac{\kappa\pi}{2}+C(\omega\tau_m)^{-\chi}\cos\frac{\chi\pi}{2}\right] , \tag{51}$$

and

$$J''(\omega)=J_\beta''+\frac{1}{G_u}\left[(\omega\tau_m)^{-\kappa}\sin\frac{\kappa\pi}{2}+C(\omega\tau_m)^{-\chi}\sin\frac{\chi\pi}{2}\right] , \tag{52}$$

where J_β' and J_β'' are given by Eqs. (27) and (28). G_R' and G_R'' are obtained by a Fourier transform of Eq. (42)

$$G_R'(\omega)=G_R\left[\sum_j\frac{\omega^2\tau_{e,j}^2}{1+\omega^2\tau_{e,j}^2}g_j\right]\Big/\sum_j g_j \tag{53}$$

and

$$G_R''(\omega)=G_R\left[\sum_j\frac{\omega\tau_{e,j}}{1+\omega^2\tau_{e,j}^2}g_j\right]\Big/\sum_j g_j . \tag{54}$$

g_j represents a Gaussian distribution of g where the statistical weight g_j of each process with time $\tau_{e,j}$ sums up to unity, i.e., $\sum_{g_j}=1$. This is a necessary simplification because L, the length of the reptation tube, itself has a distribution because the characteristics of the strands of a polymer chain are also distributed.

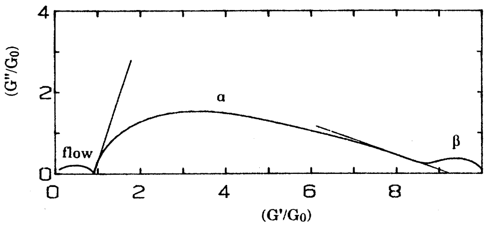

FIG. 4. Complex plane plots of the theoretically calculated G'' and G' (see text for details). The plot shows the β-, α-, and the chain disentanglement regions of a polymer.

A complex plane plot on a linear scale of the calculated values of G'' and G' is shown in Fig. 4. In it, the β process is at the highest value of G' and at the highest frequency, the large region at intermediate frequencies is the α process and the smallest region at the lowest frequencies and lowest modulus is the rubber plateau disentanglement. The values of the parameters used in the calculations are: $U=60$ kJ mol^{-1}, $\Delta U=5$ kJ mol^{-1}, $T=355$ K, $A=3\times10^{-10}$ Pa, $A_\beta=1\times10^{-10}$ Pa, $\chi=0.95$, $\kappa=0.30$, $\tau_m=8$ sec, and $(G_u/G_R)=10$. The value of (G_u/G_R) is 10^2-10^4 for most polymers, but has been used here as 10 in order to clearly show the three processes on the same plot.

VI. THE TEMPERATURE-DEPENDENT DYNAMIC-MECHANICAL BEHAVIOR

Temperature dependence of $\tau_{\max}$ for the α process, or local diffusion of a polymer chain, can be related with the temperature dependence of the time $\tau(T)$ required for a configurational transition in the Adams-Gibbs formalism[14] given by Eq. (8),

$$\tau(t)=\frac{h}{k_BT}\exp\left[\frac{B}{C_Dk_BT}\right] . \tag{55}$$

$\tau_{\max}$, being the mean time required for the diffusion leading to the loss of the local mechanical stress, is given by

$$\tau_{\max}=\frac{l}{v} , \tag{56}$$

where l is the mean distance between two regions containing the defect, and v is the velocity of diffusing molecules, given by the Stokes-Einstein equation

$$v=\frac{DF}{k_BT} . \tag{57}$$

D is the diffusion coefficient, and F is the applied local stress on a molecule or a monomer segment. Since

$$F=\frac{E}{l} , \tag{58}$$

where E is the mean elastic energy of the lines bordering the shear micro domain,

$$\tau_{\max}=\frac{l^2k_BT}{DE} . \tag{59}$$

$\tau(T)$ in Eq. (6) is related to the average distance of displacement of a monomer by,

$$\lambda^2=D\tau , \tag{60}$$

where λ is of the order of the dimension of a molcule or a monomer. Thus,

$$\tau_{\max}=\left[\frac{l}{\lambda}\right]^2\left[\frac{k_BT}{E}\right]\tau(T) . \tag{61}$$

Equations (48), (55), and (61) can be combined to give

$$\tau_m(t)=\frac{h}{E}\left[\frac{l}{\lambda}\right]^2\left[\frac{AG_u}{\kappa}\right]^{-1/\kappa}\exp\left[\frac{B}{C_Dk_BT}\right] . \tag{62}$$

For the α process at $T < T_g$ that is in the isoconfigurational glassy state, $\tau_{\max}$ is given by Eq. (31), which on substitution in Eq. (53) gives the measured relaxation time by

$$\tau_m(t) = \left[\frac{AG_u}{\kappa} \right]^{-1/\kappa} \tau_0^{1/\kappa} t_1^{(\kappa-1/\kappa)} \exp\left[\frac{U}{\kappa k_B T} \right] . \qquad (63)$$

Accordingly, at $T < T_g$, τ_m follows an Arrhenius behavior. At $T \approx T_g$, the values of τ_m of Eqs. (62) and (63) become identical, or equal to $\sim 10^4$ s. The preexponential term in Eq. (63) is $\sim 10^{-35}$ and is approximately constant in a narrow range of temperature.

The temperature dependence of the β-relaxation process is given by Eq. (22)

The calculated curves of G, J, G', G'', and $\tan\Phi$ in Figs. 1 and 2, and the calculated complex plane plot of G' and G'' in Fig. 4, have a remarkable resemblance with the experimentally measured dynamic-mechanical behavior of glasses and amorphous polymers.[5] Experimental tests for the quantitative validity of the theory for polymers are presented in a separate paper and limitations of our formalism are pointed out there. Nevertheless, it is instructive to recall that the parameter κ, χ, and μ_0 are interrelated in our theory and only one parameter μ_0 in Eq. (29) is necessary for experimentally testing its validity.

VII. EXPERIMENTAL CONSEQUENCES

An analysis of the rheological data on a variety of polymers has successfully been made by J. Y. Cavaille[32] using this theory in the glass-rubber transition range. Nevertheless, the theory leads to several other experimentally testable predictions, some of which are given below.

(1) We assumed that the concentration of defect sites remains unchanged during the viscous flow, a condition that is expected when shear propagation occurs as a result of Brownian motions. Therefore, no change in volume is anticipated as a result of the viscous flow of *a glass* at a relatively high temperature such as $T \geq 0.75\ T_g$. However, since thermal diffusion, which allows viscous flow over a long period, also allows physical aging and densification of a glass during which the number of defects, or "soft sites" decreases, the volume of a glass would slightly decrease by an amount which corresponds only to the effect of physical aging. This can be tested for two samples of a glass kept at the same temperature and for the same duration, but one under a load and the other without (for example, in zero gravity). The decrease in the volume of the two samples is expected to be the same. Furthermore, if the two samples after the above treatment are subjected to a shear stress, both should begin to yield at the same magnitude of stress which would be higher than that for the sample which was not physically aged.

(2) A quenched glass would contain a higher concentration of defect sites and therefore would begin to flow at a relatively low temperature than a normally cooled glass. This is anticipated because a larger concentration of defect sites would require a relatively small growth of shear microdomains before their merger with other similar domains nucleated at other sites.

(3) Deformation of a glass at low temperatures and high shear stresses for a period too short to allow Brownian diffusion would create quasipoint defects similar to the defects or "soft sites" considered in this theory. This may occur by one of the two mechanisms, namely, (i) creation of microloops ahead of the advancing borderlines of the microdomains[33] and (ii) the trailing of a series of sessile jogs by the expanding loops.[34] Therefore, a physically aged glass would recover its original volume and strength of β relaxation on plastic deformation of a high magnitude (such small changes in volume have now been detected, by Pixa *et al.*,[35] in a deformation range where crazing does not occur). Such a glass would also show viscous flow at a lower temperature or in a shorter time than an undeformed glass.

(4) According to Eq. (30), as $\kappa \rightarrow 1$ or $\mu_0 \rightarrow 0$, $\tau_{\max} \rightarrow \tau_1$. This means that at high temperatures where the number of soft sites is large and correlation effects are small, the α process would merge with the β process at a temperature when $\mu_0 = 0$. Thus at high temperatures, only one relaxation process is observable at $T \gg T_g$. This prediction was also made from a different but qualitative consideration[2,18] and can be tested by dielectric and mechanical relaxation measurements at sufficiently high frequencies.

(5) Since the value of the parameter χ is determined by the number of entanglements and junction points, its value should be found to decrease with increase in the number of cross links and junction points in a polymer. In general, this value should be lowest for epoxies and partially crystalline polymers, higher for entangled chains, and should be equal to 1 for molecular liquids and low-molecular weight polymers. Thus the angle of the low-frequency intercept of the complex plane plots of G^* (in Fig. 4) should depend upon the number of entanglements, junction points, and crystallinity in a polymer, and the shape of this plot should change with with the number of entanglements, junctions points, and crystallinity.

VIII. CONCLUSIONS

A theory for the rheology of the glassy state can be formulated by considering that the structure of a glass consists of randomly distributed regions of high-entropy, low- and high-density sites, or defects, with an average concentration of $\sim 10\%$ at $T < T_g$.

The defects or "soft sites" undergo shear deformation on the application of a stress. This leads to the nucleation of shear microdomains and appears as a β process. If the duration of the applied stress is long and/or the temperature is high, these microdomains enlarge through hierarchically constrained motions, so that the relaxation time is a function of time. After their extended growth, the merging of the microdomains nucleated at several sites leads to an irrecoverable macroscopic deformation or viscous flow. The premise of the theory is that β process is the precursor of the α process and viscous flow.

An extension of the theory to amorphous polymers in which the directionality of the covalent bonds restricts the number of configurational states of monomers, and in which junction points due to cross links and chain entanglements exist, can be made and the existence of both the β- and the α-relaxation processes in them can be accounted for. Several consequences of the theory can be experimentally tested by new experiments.

ACKNOWLEDGMENTS

Jean-Yves Cavaille would like to thank the Jacques-Cartier foundation for a grant. This work was further supported by a grant from the Natural Sciences and Engineering Research Council of Canada.

APPENDIX

In Eq. (42a) when $t=\tau_{f,\max}$, $\kappa(t)=\kappa$; and when $t>\tau_{f,\max}$, τ_D becomes a function of time because of the dependence of κ on t. Thus,

$$\tau_D(t)=\tau_{f,\max}=(\tau_1 t_1^{\kappa(t)-1})^{1/\kappa(t)} . \tag{A1}$$

Substituting $\kappa(t)$ in Eq. (1) from Eq. (42a),

$$\tau_D(t)=[\tau_1 t_1^{\kappa-1} t_1^{-a\kappa\delta t/\tau_{f,\max}}]^{1/\kappa(t)} , \tag{A2}$$

where

$$\delta t=t-\tau_{f,\max} . \tag{A3}$$

For small values of δt and a, Eq. (42a) may be written as

$$\frac{1}{\kappa(t)}\approx\frac{1}{\kappa}\left[1+\frac{a\delta t}{\tau_{f,\max}}\right] . \tag{A4}$$

Substituting for $\kappa(t)$ in Eq. (A2) and writing

$$x=a\delta t/\tau_{f,\max} , \tag{A5}$$

we obtain

$$\tau_D(t)=(\tau_1 t_1^{\kappa-1})^{1/\kappa}(\tau_1 t_1^{\kappa-1})^{x/\kappa}(t_1^{-x\kappa})^{(1/\kappa+x/\kappa)} . \tag{A6}$$

In Eq. (A6), when $\kappa=\kappa_0$

$$(\tau_1 t_1^{\kappa-1})^{1/\kappa}=\tau_{f,\max} \tag{A7}$$

and

$$(\tau_1 t_1^{\kappa-1})^{x/\kappa}=\tau^{x}_{f,\max} . \tag{A8}$$

Therefore,

$$\tau_D(t)=\tau^{1+x}_{f,\max}(t_1^{-(x+x^2)}) , \tag{A9}$$

when x is small, x^2 is negligible and, therefore, we may write

$$\tau_D(t)=\tau^{1+x}_{f,\max}t_1^{-x} , \tag{A10}$$

or

$$\tau_D(t)=\tau_{f,\max}(\tau_{f,\max}/t_1)^{x} , \tag{A11}$$

or

$$\tau_D(t)=\tau_{f,\max}\exp[x\ln(\tau_{f,\max}/t_1)] . \tag{A12}$$

Since x is small, the exponential in Eq. (A12) may be written as, $(1+x\ln\tau_{f,\max}/t_1)$ and thus

$$\tau_D(t)\approx\tau_{f,\max}\left[1+x\ln\left[\frac{\tau_{f,\max}}{t_1}\right]\right] . \tag{A13}$$

Now, replacing x by its original formula in Eq. (A5), and writing for

$$b=a\ln(\tau_{f,\max}/t_1) , \tag{A14}$$

$$\tau_D(t)\approx\tau_{f,\max}\left[1+\frac{b\delta t}{\tau_{f,\max}}\right] . \tag{A15}$$

Since a is small, and if δt is also small,

$$\left[1+\frac{b\delta t}{\tau_{f,\max}}\right]\approx\left[1+\frac{\delta t}{\tau_{f,\max}}\right]^{b} , \tag{A16}$$

Eq. (A12) becomes

$$\tau_D(t)\approx\tau^{1-b}_{f,\max}(\tau_{f,\max}+\delta t)^{b} . \tag{A17}$$

Substituting for δt from Eq. (A3),

$$\tau_D(t)\approx\tau^{1-b}_{f,\max}t^{b} . \tag{A18}$$

We define a quantity χ as

$$\chi=(1-b) , \tag{A19}$$

so that by substituting for χ in Eq. (A15),

$$\tau_D(t)\approx\tau^{\chi}_{f,\max}t^{1-\chi} , \tag{A20}$$

where $\tau_{f,\max}$ is the time at which shear microdomain begin to merge. For $t<\tau_{f,\max}$, κ is constant and can be measured by the high-frequency intercept of the complex plane plot in Fig. 4.

---

[*] Previous address: McMaster University, Hamilton, Ontario, Canada L8S 4L7.

[1] J. Perez, Rev. Phys. Appl. **21**, 93 (1986).

[2] G. P. Johari, in *Plastic Deformation of Amorphous and Semicrystalline Materials*, 1982 Les Houches Lectures (Les Editions de Physique, Paris, 1982), pp. 109–141.

[3] J. Perez, J. Y. Cavaille, S. Etienne, F. Fouquet, and F. Guyot, Ann. Phys. **8**, 417 (1983).

[4] R. G. Palmer, D. L. Stein, E. Abrahams, and P. W. Anderson, Phys. Rev. Lett. **53**, 958 (1984).

[5] J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York 1980).

[6] J. Perez, Polymer **29**, 483 (1988).

[7] J. Perez, J. Y. Cavaille, S. Etienne, and C. Jourdan, Rev. Phys. Appl. **23**, 125 (1988).

[8] M. H. Cohen and D. Turnbull, J. Chem. Phys. **31**, 1164 (1959); **34**, 120 (1961).

[9] M. H. Cohen and G. S. Grest, Phys. Rev. B **20**, 1077 (1979); **21**, 4113 (1980).

[10] M. H. Cohen and G. S. Grest, Solid State Commun. **39**, 143

(1981).
[11]R. E. Robertson, R. Simha, and J. G. Curro, Macromolecules **17**, 911 (1984).
[12]S. A. Brawer, J. Chem. Phys. **81**, 954 (1984).
[13]J. C. Dyre, Phys. Rev. Lett. **58**, 792 (1987).
[14]G. Adams and J. W. Gibbs, J. Chem. Phys. **43**, 139 (1965).
[15]D. Srolovitz, K. Maeda, V. Vitek, and T. Egami. Philos. Mag. **44**, 847 (1981).
[16]C. Cunat, Ph. D. thesis, Universite de Nancy, 1985.
[17]G. P. Johari and M. Goldstein, J. Chem. Phys. **53**, 2372 (1970).
[18]G. P. Johari, J. Chem. Phys. **58**, 1766 (1973).
[19]J. Perez, Acta Metall. **32**, 1163 (1984).
[20]R. Kohlrausch, Ann. Phys. (Leipzig) **12**, 393 (1887).
[21]G. Williams and D. C. Watts, Trans. Faraday Soc. **66**, 80 (1970).
[22]K. L. Ngai and C. T. White, Phys. Rev. B **20**, 2475 (1979).
[23]L. A. Dissado and R. M. Hill, Proc. R. Soc. London, Ser. A **30**, 131 (1983).
[24]K. L. Ngai, A. K. Jonscher, and C. T. White, Nature **277**, 185 (1979).
[25]K. L. Ngai, R. W. Rendall, A. K. Rajagopal, and S. Teitler, Ann. N. Y. Acad. Sci. **484**, 150 (1986).
[26]J. T. Bendler and M. F. Schlesinger, Macromolecules **18**, 591 (1985).
[27]R. Rammal, J. Phys. **46**, 1837 (1985).
[28]V. S. Dotsenko, J. Phys. C **18**, 6023 (1985).
[29]C. Hong, W. Xiang, and F. Jun-xin, J. Phys. C **19**, L499 (1986).
[30]M. Doi and S. F. Edwards, J. Chem. Soc. Faraday Trans. II **74**, 818 (1978); **74**, 1789 (1978); **74**, 1882 (1978).
[31]P. G. deGennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, 1979).
[32]J. Y. Cavaille, Ph.D. thesis, Institut National des Sciences Appliquees de Lyon, 1987.
[33]B. Escaig (unpublished).
[34]C. G'Sell, J. Perez, J. Y. Cavaille, H. El Bari, and G. P. Johari, Mater. Sci. Eng. (to be published).
[35]R. Pixa, M. Rousse, and C. Wippler (unpublished).