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Dynamics in glassy polymers: The Eyring model revisited

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Applying a stress to a glassy polymer accelerates its dynamics as one goes from low stress up to plastic regime. For decades, the phenomenological Eyring's model has been used to describe plastic flow in polymers. This model, however, raises fundamental issues which makes its use deleterious in glassy polymers. We propose an alternative model in which the elastic energy stored at the length scale of dynamical heterogeneities $\xi \approx 3$–5 nm reduces the free energy barrier for relaxation. Contrary to the Eyring's activation volume, which has no clear interpretation, this length scale is derived from physical arguments, based on a detailed account of relaxation mechanisms at the molecular scale. Recent creep experiments in glassy polymers by Ediger and coworkers allow for discriminating the two pictures. It is shown that the whole evolution of the τ_α relaxation time under stress can be reproduced quantitatively, using as the only adjustable parameter the scale ξ. The obtained value of ξ is the same as the value previously determined by considering the whole set of properties of glassy polymers. This confirms the coherence and completeness of the theory of relaxation processes in nonpolar glassy polymers that we proposed in previous works.

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I. INTRODUCTION

Mechanical and dynamical properties of polymers have been intensively studied for a long time due to their fundamental and technological importance [1–3]. When strained at a given strain rate, beyond the elastic regime, glassy polymers exhibit a maximum in the stress-strain curves—a so-called yield point—at a strain of a few percents and typical yield stress values of a few tens of MPa's [3]. Beyond this maximum, the stress drops by a few tens of MPa (strain-softening regime) before it reaches a plateau corresponding to plastic flow. Strain-hardening may then occur at even larger strain, depending on molecular weight and cross-linking [4].

The fact that yield stress and plastic flow result from a stress-induced acceleration of the dynamics at the molecular level has been demonstrated by recent experiments in which the microscopic dynamics were probed under stress [5–12]. Molecular dynamics simulations also support the fact that the dynamics is enhanced during plastic deformation [13,14]. On the other hand, the dynamics is known to be strongly heterogeneous in the vicinity of T_g [15–18]. This results in nonexponential relaxation moduli, characterized by a so-called stretching exponent β smaller than 1. Experiments have shown that β increases during uniaxial extension, which indicates that the dynamics become more homogeneous during plastic deformation than at rest [7].

The first generic model proposed for describing plastic deformation has been the Eyring model [19], in which a thermally activated motion across a free energy barrier is biased by the flow. While the free energy barrier itself is not affected by the applied stress, it is quite often (mis)interpreted as a change of the effective free energy barrier in the regime of plastic flow or at yield, wherein it is usually used [4,20,21]. In the Eyring model, the effect of the stress on the dynamics is controlled by the so-called activation volume v. The activation volume is a fitted parameter determined *a posteriori* from the observed variation of the dynamics under stress. It has no clear physical interpretation or relationship to material parameters and simply reflects in a heuristic way the sensitivity of the yield stress value on the strain rate [22,23].

In this context, a detailed description of the dynamics during plastic deformation from the molecular level up to the scale of a few tens of nanometers is crucially needed [25,26]. The mesoscale model denoted "Percolation of Free Volume Distribution" (PFVD) model (according to Ref. [27]) has been developed to describe nonpolar polymer glasses [28–31]. In this model, the heterogeneous dynamics is described at the scale of subunits ("dynamical heterogeneities") of size ξ typically 3–5 nm, based on a detailed account of relaxation mechanisms at the molecular scale, whose competition sets the scale ξ. In fact, this scale plays a central role in the model. It must be emphasized that it is determined from physical arguments and has been found to be perfectly consistent with experimental measurements [16]. It was demonstrated that the PFVD model provides a unified explanation for a full set of apparently distinct properties of glassy polymers, namely linear viscoelasticity [32,33], small probe diffusion and Stokes's law violation [29], the effect of confinement [28,32,34,35] and of hydrostatic pressure [36] on T_g, the ageing and rejuvenating kinetics upon heating [29,30] and the yield stress [1,24,37].

In the PFVD model, nonlinear mechanical properties of glassy polymers are related to the distribution and evolution of dynamical heterogeneities from equilibrium up to plastic deformation. The model can be solved by numerical simulations and macroscopic time scales can be reached. In contrast with the Eyring model, it is assumed that the applied stress not only biases the motion but also reduces the free energy barriers between elementary jumps [24].

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The effect of the applied stress on the distribution of relaxation times is actually difficult to characterize experimentally in the yield regime, and direct measurements are rare. In Refs. [7,9], the evolution of the main relaxation time τ_α has been measured during creep (controlled stress) experiments. In other experiments aimed at measuring the evolution of the whole distribution, only a part of it was accessible [8,11].

II. DESCRIBING THE GLASS TRANSITION: DYNAMICAL HETEROGENEITIES, FACILITATION

In this paper, we report on a spectacular outcome of the PFVD model, namely the quantitative modeling of experimental results on the microscopic dynamics under plastic deformation published by Ediger and coworkers [7], without any further adjustable parameter.

Within the generic framework of the free volume model, in van der Waals liquids or molten polymers, the decrease of free volume on cooling results in a slowing down of the relaxation time τ_α which dominates the mechanical behavior at long times, according to the semi-empirical Williams Landel Ferry (WLF) law [2] $\tau_\alpha = \tau_0 \exp(\Theta/\tilde{\epsilon})$, where Θ is a number of order unity and $\tilde{\epsilon}$ is the dynamical free volume fraction [29,30].

It has long been proposed that α-relaxation is a collective effect which takes place on some cooperative scale ξ [38]. The basic assumption of the PFVD model is that density (free volume) fluctuations at scale $\xi \approx 3$–5 nm generate a wide distribution of relaxation times according to the WLF law. The sample may be viewed as a collection of dynamical subunits of volume ξ^3, containing an average number $N_c = \xi^3/a^3$ monomers. Considering the bulk modulus value, density fluctuations on scale ξ are $\sim\pm 1\%$ [28–31]. Within the free volume picture, α-relaxation results from the packing of N_c monomers, in such a way that a volume of order a^3 (the monomer volume) is made available for one particular monomer to move one step away [28,29]. By writing $\tau_\alpha = \tau_0 \exp[\Delta F_0(T)/T]$ with $\tau_0 \approx 10^{-13}$ s a molecular jump attempt (collision) frequency, it follows that the overall free energy barrier $\Delta F_0(T)$ for α-relaxation, resulting from this cooperative packing of N_c monomers, is of order $30T$ at rest close to T_g, where T, the temperature expressed in Joule, is of order 4–5 $\times 10^{-21}$ J.

The core of the model is then the determination of the scale ξ. Individual molecular jumps are controlled by two distinct processes (Fig. 1) [29–31]: (1) Internal reorganization within a subunit, with the characteristic time τ_{int}, related to local free volume by the WLF law; (2) if τ_{int} happens to become very long, in a very dense subunit, this last may dissolve much faster (time τ_{diff}) by diffusion in faster neighboring subunits (*facilitation process*). As the size decreases, τ_{int} may become increasingly long since the amplitude of density fluctuations increases, while, conversely, τ_{diff} becomes faster. The size ξ is then determined self-consistently by the competition of these two distinct relaxation mechanisms: ξ (or N_c) is the smallest scale at which the lifetime of density fluctuations can be equal to or larger than τ_α [29,30]. This competition is illustrated in Fig. 1.

The generic concept of *facilitation*, i.e., the idea that local mobility may be accelerated by a faster environment, is not recent [39,40]. The above argument, based on free volume diffusion from neighboring faster subunits, gives an explicit picture of this concept. As a consequence of the facilitation mechanism, the size $\xi = aN_c{}^{1/3}$ also sets the effective width of the relaxation time distribution, between τ_α (the long time cutoff) and a short time limit τ_f, according to $\tau_\alpha = N_c^{2/3}\tau_f$. This relation means that relaxation of the slowest subunits corresponds both to internal processes and to melting by the faster environment. The temporal asymmetry of the rejuvenation and ageing dynamics in glassy polymers is a direct manifestation of the facilitation mechanism [30,31,41]. The macroscopic behavior of a system, and specifically the macroscopic relaxation time τ_α, is then the relaxation time of the slowest subunits which percolate, i.e., which are able to transmit the rigidity within a system.

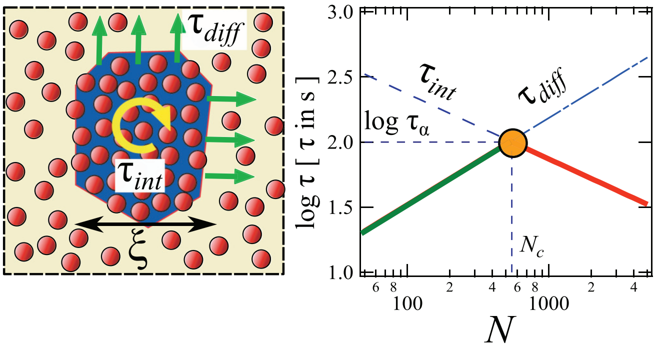

FIG. 1. Left: A slow (high density) subunit of size $\xi \sim 3$–5 nm within a faster (lower density) surrounding may relax either by internal free volume reorganization (time τ_{int}) or diffusion (time τ_{diff}) (density differences are exaggerated). Right: Variation of $\tau_{\text{int}} \sim N^{-1/2}$ (dashed curve) and $\tau_{\text{diff}} \sim N^{2/3}$ (dash-dotted curve) vs the number N of monomers in subunits.

N_c was calculated to be of order 1000 monomers, or equivalently $\xi \simeq 3$–5 nm [29], in remarkable agreement with NMR experiment results [16]. A major outcome of our approach is that many different features, such as the Stokes's law violation [29], T_g shifts in confinement [28,32,34,35] and related reinforcement effects in filled elastomers [32,42], the yield and plastic flow of glassy polymers [24], may be explained using the same or similar values of $N_c \approx 1000$ at T_g, as extensively discussed in Ref. [31].

III. THE CLASSICAL EYRING PICTURE

In the Eyring model [19], the diffusion of molecules or monomers is biased by the applied stress, while the free energy barrier between two consecutive states ΔF_0, and hence the relaxation time τ_α, is not affected. The shear rate (flux) $\dot{\gamma}$ is given as a function of the stress σ by

$$\dot{\gamma} = \frac{1}{\tau_0} \exp\left(-\frac{\Delta F_0}{T}\right) \sinh \frac{\sigma v}{T}, \tag{1}$$

where v is the so-called activation volume and $\tau_\alpha = \tau_0 \exp(\Delta F_0/T)$ the dominant relaxation time τ_α in the absence of stress. τ_0 is a microscopic time which must be of order 10^{-12} s if the function in the exponential is properly interpreted as a free energy barrier, as it is done here. This expression is the standard result of the Eyring model which is currently used in the literature for describing plastic yield and flow such as in Ref. [43]. The temperature dependance of this free energy barrier, which contains enthalpic and entropic contributions, may be complex. In particular, the entropic contribution may lead to *apparent* values of the microscopic time τ_0 dramatically smaller than 10^{-12} s. This point of view is a standard approach in the literature when the α-relaxation is described in the context of an energy, or more properly, a free energy-landscape [44,45].

The model is not aimed at calculating the free energy barriers, which, for instance, would be required for computing the WLF parameters. The only assumption made here is that the stress affects the free energy barrier, in a way which is described below.

Note that even though polymers close to or below T_g exhibit very broad relaxation time distributions, a dominant relaxation time in mechanical or dielectric experiments, denoted τ_α, can always be defined by integrating a properly normalized relaxation function to infinity. This is a classical issue discussed, e.g., in Refs. [46] and [31].

In the small stress limit, the expression $\eta = \sigma/\dot{\gamma} \approx T\tau_\alpha/v$ is obtained for the viscosity. On the other hand, the viscosity is given by $\eta \approx K\tau_\alpha$ where K is the high frequency storage modulus in the glassy state. Therefore, in the linear regime, K should be related to the activation volume by $v = T/K$. With $K \approx 4 \times 10^9$ Pa typically, this would give a volume $v' \approx 10^{-3}$ nm^3, of the order the atomic volume, while the Eyring's activation volume, determined in the plastic flow regime, is usually found to be $v \sim 1$ nm^3. There is thus a discrepancy of typically three orders of magnitude between the plastic and linear regimes in the standard Eyring model.

IV. THE PFVD MODEL: ACCELERATION OF THE DYNAMICS UNDER STRESS, YIELD

It is experimentally known that relaxation is accelerated with respect to the equilibrium rate τ_α^{-1} when a large enough stress is applied on a glassy material [3,6–12]. This implies that the local relaxation time is not a function of the local density only, but must also depend on the local stress. Our central assumption is that the stress, besides biasing molecular motion [Eq. (1)], also lowers the free energy barrier ΔF_0, which results in shorter time scales. As explained in Ref. [24], this change *must be quadratic*. It is *not* contained in the Eyring model.

The free energy barrier ΔF_0 for a local change of configuration (α relaxation) is decreased by an amount corresponding to the strain energy stored in the material at the scale ξ, leading to a new free energy barrier under stress of the form

$$\Delta F(T,\sigma) = \Delta F_0(T) - \frac{\xi^3}{2}\frac{\sigma:\sigma}{G_0'}, \tag{2}$$

where the quantity $\sigma{:}\sigma$ is defined as $\sigma{:}\sigma = (1/2)[(\sigma_1-\sigma_2)^2 + (\sigma_2-\sigma_3)^2 + (\sigma_3-\sigma_1)^2]$ with $\sigma_1, \sigma_2, \sigma_3$ the eigenvalues of σ, the local (deviatoric) stress tensor. This expression, analogous to a von Mises criterium, is a scalar. It is the only quadratic function of the stress tensor which is invariant by rotation and vanishes when the stress is zero or isotropic. Apart from a pressure term, this term is the first term in a series expansion describing how a scalar can change under an applied stress. This term is sufficient for discussing the experiments by Ediger *et al.* [7]. This expression may be extended to take the effect of pressure into account [36], which shall be done in further extension of this model.

It follows that the relation between the shear rate and the stress [Eq. (1)] is modified into [24]

$$\dot{\gamma} = \frac{1}{\tau_0}\exp\left(-\frac{\Delta F_0}{T} + \frac{\xi^3\sigma:\sigma}{2KT}\right)\frac{\sigma v'}{T}. \tag{3}$$

This expression for plastic flow differs from the standard Eyring model [Eq. (1)] in two distinct ways. First, the argument of the exponential (the free energy barrier) is decreased by the term quadratic in σ. Second, in the Eyring-like term $\sinh \sigma v'/T$, which is necessary to bias the flow and describe linear flows analytically, the volume $v' = T/K \sim 10^{-3}$ nm^3 is typically three orders of magnitude smaller than the standard Eyring's activation volume, generally measured experimentally in the yield regime.

With $\sigma \approx 5 \times 10^7$ Pa at most, the quantity $\sigma v'/T$ in Eq. (3) is always smaller than about 10^{-2} and the sinh term can be safely linearized. Thus, we obtain that the strain rate, which is a tensor, is given by a scalar (the inverse of the relaxation time) multiplied by the tensor $\sigma v'/T$.

Equation (3) then gives the viscosity $\eta = \sigma/\dot{\gamma}$, and therefore the τ_α relaxation time, as a function of the applied stress in an explicit form

$$\tau(T,\sigma) = \tau_\alpha(T)\exp\left(-\frac{\xi^3}{2T}\frac{\sigma:\sigma}{G_0'}\right), \tag{4}$$

where $\tau_\alpha(T)$ is the relaxation time in the absence of stress.

It is important to note that the change of free energy barrier at yield *per monomer*, as compared to the thermal energy T, $\delta f/T = a^3\sigma:\sigma/(2TK)$ is very small, of order 10^{-2}. Would relaxation take place at a monomer scale, the yield stress values would be considerably larger than observed experimentally. Conversely, at the scale of N_c monomers (or equivalently at the scale ξ^3), the decrease of free energy barrier $N_c\delta f/T = \xi^3\sigma:\sigma/(2TK)$ is of order 10. It follows that the free energy barrier for relaxation drops from, e.g., $40T$ to $30T$ and may therefore be crossed on the experimental timescale. The effect thus becomes important because α-relaxation corresponds to collective reallocation of free volume at the scale of N_c monomers. This scale corresponds as well to the correlation scale of the dynamics [29,30]. In a very slow subunit which does not relax, monomers do not move. Conversely, in a neighboring fast subunit, monomers may move cooperatively in the direction associated to the applied stress. The free energy cost for creating a vacuole of one monomer volume through cooperative motion of N_c monomers is thereby reduced by the amount $N_c\delta f$.

Contrary to α-relaxation, the so-called secondary β-relaxation is generally not modified at stress values corresponding to yield [8,11]. This is a further illustration of the importance of the characteristic scale ξ. Indeed, β-relaxation takes place on a very small scale, typically the scale of one chemical bond or atom, of order $\delta v \sim 10^{-30}$m^3, and, as mentioned above, the elastic energy stored under stress at this scale is negligible with respect to thermal energy. On the other hand, the β-process may in some cases be necessary for the α-process to occur. In such cases, should the β-process be slower than the experiment timescale, as it may be the case in impact tests, then the α-process would be inhibited, which would inhibit plastic flow and make the material brittle [49].

A critical stress value $\sigma_c{}^2 = 2KT/\xi^3$ may be defined from Eq. (4). When $\sigma{:}\sigma \ll \sigma_c{}^2$(linear regime), the equilibrium distribution of relaxation times is not modified and $\tau(\sigma) \approx \tau_\alpha$. The distribution of relaxation times starts to deviate from equilibrium, and mechanical rejuvenation is induced, when $\sigma{:}\sigma \sim \sigma_c{}^2$. Using $2T \approx 10^{-20}$ J, $K \approx 3 \times 10^9$ Pa, and $\xi^3 \approx 10^{-25}$ m^3 (which corresponds to $\xi = 5$ nm) gives a typical value $\sigma_c \approx 1 - 2 \times 10^7$ Pa, which corresponds to the onset of stress induced softening, obtained *without any additional adjustable parameter*.

Though our model describes relaxation under stress in a different way, it may be mapped on the Eyring model by giving a physical interpretation to the activation volume. At the yield stress σ_y, the dominant relaxation time [Eq. (4)] becomes of order $\dot{\gamma}^{-1}$, which relates the yield stress σ_y to the parameters K, ξ and $\tau_\alpha(T)$: $\sigma_y{}^2 = (2KT/\xi^3)\ln[\dot{\gamma}\tau_\alpha(T)] = \sigma_c{}^2\ln[\dot{\gamma}\tau_\alpha(T)]$. Below T_g, as typically $\ln[\dot{\gamma}\tau_\alpha(T)] \approx 10$, $\sigma_y \approx 5 \times 10^7$ Pa, which is the correct value of the yield stress. On the other hand, in the Eyring model [Eq. (1)], approximating $\sinh \sigma v/T \approx \exp \sigma v/T$ (as $\sigma v/T \sim 10$ close to the yield stress) gives $\sigma_y = (T/v)\ln[\dot{\gamma}\tau_\alpha(T)]$. Eliminating $\ln[\dot{\gamma}\tau_\alpha(T)]$ then gives $v = \sigma_y\xi^3/K \approx 3\sigma_c\xi^3/K \approx 3(2T/K)^{1/2}\xi^{3/2}$, which would correspond to the standard Eyring's activation volume calculated from our model. A value $v \approx 1 - 2$ nm^3, typical for glassy polymer plasticity, is obtained.

V. A COMPARISON WITH EXPERIMENTAL DATA

The effect of stress on the relaxation time distribution is difficult to measure in the yield regime [11]. In Ref. [7], the authors measured the molecular mobility in a poly(methyl methacrylate) glass during tensile deformation following a fixed stress (creep) protocol. The dominant relaxation time τ_c is calculated by integrating the orientation correlation function of a fluorescent probe up to infinity. This relaxation time is equivalent to the mechanical relaxation time τ_α, as assumed by the authors of Ref. [7] and discussed in Refs. [31,46]. This timescale is given by the corresponding WLF law of the considered polymer [47]. Lee *et al.* used the Eyring model for fitting the small deformation regime, which, as mentioned above, is not the usual use of this model. They relate the relaxation time τ_α to the stress through the expression for the viscosity $\tau_\alpha \sim \eta = \sigma/\dot{\gamma} \sim \sigma/\sinh(\sigma v/T)$, where the last equality comes from Eq. (1). They find an Eyring's activation volume v varying from 2.7 nm^3 at 375.7 K to 4.4 nm^3 at 385.7 K. These data, together with the Eyring model fitting, are plotted in Fig. 5 of Ref. [7]. Two problems are apparent. First, in addition to the Eyring's activation volume, an ad-hoc, arbitrary prefactor of order 10^2–10^3 is needed to recover the equilibrium τ_c value at zero stress due to the discrepancy when extrapolating the Eyring's equation adjusted in the yield regime to small stress, as mentioned above. Second, upon increasing the stress into the non linear (plastic flow) regime, the fit tends towards a linear variation of the relaxation time with the stress, while experimental data follow a stronger, nonlinear variation. The authors indeed acknowledged that the fit is limited to the small stress regime. Actually, for the lowest considered temperature, the fit is correct when τ_c has decreased by less than a factor of 3 only, while it decreases by two to three orders of magnitude over the whole measured stress range.

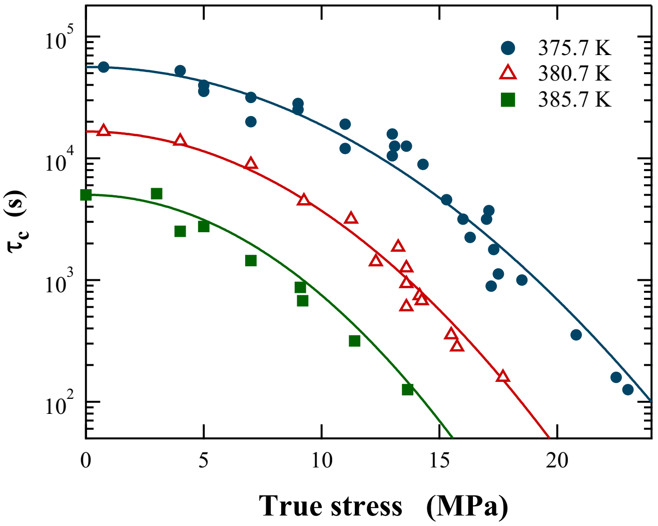

FIG. 2. The data points are the experimental results by Lee *et al.* [7]. Continuous curves through have been calculated by Eq. (4) with the constant values $\xi = 5$ nm and a bulk modulus $G_0' = 2 \times 10^9$ Pa. A prefactor μ is used in the argument of the exponential ($\mu = 1.0$ at 375.7 K, 1.26 at 380.7 K, and 1.61 at 385.7 K).

Equation (4) was used to fit the microscopic dominant relaxation time τ_α, as directly measured in Ref. [7]. Parameter values $G_0' = 2$ GPa and $\xi = 5$ nm were used. Note that the bulk modulus G_0' varies with temperature. The temperature dependance of the bulk modulus for PMMA has been reported and analyzed in Ref. [28]. It varies by about 20% over the 10 K range investigated here [7]. To fit the data, the value of the modulus was kept constant while instead a prefactor μ was introduced in the argument of the exponential in Eq. (4). The data are reproduced by using the values $\mu = 1.0$ at 375.7 K, 1.26 at 380.7 K, and 1.61 at 385.7 K. If we take the variation of the bulk modulus with temperature into account, we still need a correction factor $\mu \approx 1.3$. These values are very close to 1 and the trend is in qualitative agreement with the temperature variation of the modulus. This correction may be due to yet unknown mechanisms which would appear as corrections to the main picture presented here which capture the right order of magnitude of the effects.

The measured variation of the relaxation time τ_α is perfectly reproduced over the entire stress range, without any additional adjustable parameter other than ξ. The value $\xi \approx 5$ nm is fully consistent with other estimates (Fig. 2). Different values of ξ^3 would lead to strong discrepancies in the variation of τ_α as compared to the data in Fig. 2. This validates further our estimate of the size ξ^3 (or equivalently N_c) of dynamical heterogeneities, which can thus be determined in a quite precise way from experimental data.

Other so-called free energy landscape approaches similar to our approach have been proposed in the literature. According to Maloney and Lacks, the change of free energy barrier should be given by an expression of the type $(F_c - F)^{3/2}$, where F is a quantity proportional to the applied stress [48]. The resulting change in free energy barrier was plotted in Fig. 5 of Ref. [48] as a function of the stress. This function can certainly not account for the experimental data by the Ediger group in Ref. [7]. While measurement results give a concave curve, i.e., with a positive second derivative, and zero slope at the origin, the model by Maloney and Lacks predicted a negative slope at origin and a positive second derivative. Fan and Egami as well considered a free energy landscape model [44,45]. They proposed that the change in free energy barrier is quadratic for the β-relaxation, in a way similar to what we propose for the α-relaxation. However, for the α-relaxation, they assumed that the change is proportional to $-\sigma^{3/2}$ (which is different from the model by Maloney and Lacks). It is not possible either to reproduce the data by the Ediger group in a satisfactory way with this variation, which does not provide a better fit than the Eyring model used in Ref. [7]. In addition, the model by Fan and Egami does not provide any physical insight for the prefactor, which our model does.

VI. CONCLUSION

Finally, to describe relaxation mechanisms in glassy polymers under strain, we proposed an alternative way to considering the coupling between the stress and the dynamics. We propose that local free energy barriers for α-relaxation are lowered as a consequence of the elastic energy stored on the scale ξ of dynamical heterogeneities. When this process is combined with facilitation and local ageing dynamics, the full evolution of the relaxation time distribution can be computed as a function of temperature, strain, and strain rate, or more generally during a complex thermomechanical history, using as the only adjustable parameter the scale ξ^3. In fact, due to similar local relaxation (melting) mechanisms, the evolutions of the dynamics upon stretching or upon heating a glassy polymer are very similar [30,37].

The power of the model has been demonstrated by the fact that a number of apparently distinct phenomena occurring in glassy polymers are explained in a unified way, with essentially only one adjustable parameter, namely the size ξ of dynamical heterogeneities. In contrast with the Eyring's activation volume, the volume ξ^3 is estimated from physical arguments. It is effectively at the core of dominant relaxation mechanisms in glassy polymers [24,31]. The scale ξ plays a double key role in the model, first, for calculating the decrease of free-energy barriers and, second, for calculating the dynamical coupling between neighboring subunits. The present paper shows that experiments on the dynamics under stress by Ediger and coworkers [7] effectively provide a measurement of the scale of dynamical heterogeneities, which is found to be 5 nm in their experiments.

That a small applied stress results in an acceleration of the dynamics is an experimental fact observed in all mechanical experiments on the yield of glassy polymers. This effect was quantitatively measured in the experiments by Ediger *et al.* [7]. This is that very experimental fact that needed to be explained. The explanation we give is that the α-relaxation involves free energy changes which are small on the monomer scale, but are associated to the coherent motion of a large number N_c of monomers. Both the low yield stress values observed in glassy polymers and the experimental results by the Ediger group are indeed consistent with the fact that the α-relaxation involves a large number of monomers. Typical yield stress values correspond to a free energy change per monomer of order $0.01T$ at yield, which corresponds to typically $10T$ at yield on the scale relevant for the α-relaxation. On the contrary, the β-relaxation in polymers, which is essentially insensitive to the applied stress [49] involves motion on a very small scale.

[1] R. N. Haward, *The Physics of Glassy Polymers* (Applied Science, London, 1973).

[2] J. D. Ferry, *Viscoelastic Properties of Polymers* (John Wiley and Sons, New York, 1980).

[3] L. E. Nielsen and R. F. Landel, *Mechanical Properties of Polymers and Composites* (Marcel Dekker, New York, 1994).

[4] H. E. H. Meijer and L. Govaert, Mechanical performance of polymer systems: The relation between structure and properties, Prog. Polym. Sci. **30**, 915 (2005).

[5] L. S. Loo, R. E. Cohen, and K. K. Gleason, Chain mobility in the amorphous region of nylon 6 observed under active uniaxial deformation, Science **288**, 116 (2000).

[6] H.-N. Lee, K. Paeng, S. F. Swallen, and M. D. Ediger, Direct measurement of molecular mobility in actively deformed polymer glasses, Science **323**, 231 (2009).

[7] H.-N. Lee, K. Paeng, S. F. Swallen, M. D. Ediger, R. A. Stamm, G. A. Medvedev, and J. M. Caruthers, Molecular mobility of poly(methyl methacrylate) glass during uniaxial tensile creep deformation, J. Polym. Sci., Polym. Chem. Ed. **47**, 1713 (2009).

[8] J. Kalfus, A. Detwiler, and A. J. Lesser, Probing segmental dynamics of polymer glasses during tensile deformation with dielectric spectroscopy, Macromolecules **45**, 4839 (2012).

[9] B. Bending, K. Christison, J. Ricci, and M. D. Ediger, Measurement of segmental mobility during constant strain rate deformation of a poly(methyl methacrylate) glass, Macromolecules **47**, 800 (2014).

[10] B. Bending and M. D. Ediger, Molecular mobility of poly(methyl methacrylate) glass during uniaxial tensile creep deformation, J. Polym. Sci., Polym. Chem. Ed. **54**, 1957 (2016).

[11] R. Pérez-Aparicio, D. Cottinet, C. Crauste-Thibierge, L. Vanel, P. Sotta, J.-Y. Delannoy, S. Ciliberto, D. R. Long, Dielectric spectroscopy of a stretched polymer glass: Heterogeneous dynamics and plasticity, Macromolecules **49**, 3889 (2016).

[12] K. Hebert and M. D. Ediger, Reversing strain deformation probes mechanisms for enhanced segmental mobility of polymer glasses, Macromolecules **50**, 1016 (2017).

[13] R. A. Riggleman, H.-N. Lee, M. D. Ediger, and J. J. de Pablo, Free Volume and Finite-Size Effects in a Polymer Glass under Stress, Phys. Rev. Lett. **99**, 215501 (2007).
[14] R. A. Riggleman, H.-N. Lee, M. D. Ediger, and J. J. de Pablo, Heterogeneous dynamics during deformation of a polymer glass, Soft Matter **6**, 287 (2010).
[15] M. T. Cicerone, F. R. Blackburn, and M. D. Ediger, Anomalous diffusion of probe molecules in polystyrene evidence for spatially heterogeneous segmental dynamics, Macromolecules **28**, 8224 (1995).
[16] U. Tracht, M. Wilhelm, A. Heuer, H. Feng, K. Schmidt-Rohr, and H. W. Spiess, Length Scale of Dynamic Heterogeneities at the Glass Transition Determined by Multidimensional Nuclear Magnetic Resonance, Phys. Rev. Lett. **81**, 2727 (1998).
[17] M. D. Ediger, Spatially heterogeneous dynamics in supercooled liquids, Annu. Rev. Chem. **51**, 99 (2000).
[18] S. A. Reinsberg, X. H. Qiu, M. Wilhelm, H. W. Spiess, and M. D. Ediger, Length scale of dynamic heterogeneity in supercooled glycerol near T_g, J. Chem. Phys. **114**, 7299 (2001).
[19] H. Eyring, Viscosity, plasticity, and diffusion as examples of absolute reaction rates, J. Chem. Phys. **4**, 283 (1936).
[20] C. Bauwens-Crowet, J. C. Bauwens, and G. Homes, Tensile Yield Stress Behaviour of Glassy Polymers, J. Polym. Sci., A-2 **7**, 735 (1969).
[21] I. M. Ward, Review - Yield behavior of polymers, J. Mat. Sci. **6**, 1397 (1971).
[22] K. Chen and K. S. Schweizer, Stress-enhanced mobility and dynamic yielding in polymer glasses, Europhys. Lett. **79**, 26006 (2007).
[23] K. Chen and K. S. Schweizer, Microscopic constitutive equation theory for the nonlinear mechanical response of polymer glasses, Macromolecules **41**, 5908 (2008).
[24] A. Dequidt, L. Conca, J. Y. Delannoy, P. Sotta, F. Lequeux, and D. R. Long, Heterogeneous dynamics and polymer plasticity, Macromolecules **49**, 9148 (2016).
[25] K. S. Schweizer and E. J. Saltzman, Theory of dynamic barriers, activated hopping, and the glass transition in polymer melts, J. Chem. Phys. **121**, 1984 (2004).
[26] K. Chen and K. S. Schweizer, Theory of yielding, strain softening, and steady plastic flow in polymer glasses under constant strain rate deformation, Macromolecules **44**, 3988 (2011).
[27] K. Chen, E. J. Saltzman, and K. S. Schweizer, Segmental dynamics in polymers: From cold melts to ageing and stressed glasses, J. Phys.: Condens. Matter **21**, 503101 (2009).
[28] D. Long and F. Lequeux, Heterogeneous dynamics at the glass transition in van der Waals liquids, in the bulk and in thin films, Eur. Phys. J. E **4**, 371 (2001).
[29] S. Merabia and D. Long, Heterogeneous dynamics at the glass transition in van der Waals liquids: Determination of the characteristic scale, Eur. Phys. J. E **9**, 195 (2002).
[30] S. Merabia and D. Long, Heterogeneous dynamics, aging and rejuvenating in van der Waals liquids, J. Chem. Phys. **125**, 234901 (2006).
[31] A. Dequidt, D. R. Long, S. Merabia, and P. Sotta, Mechanical properties of polymers and nanocomposites close to the glass transition, *Polymer Glasses*, edited by C. Roth (Taylor and Francis, Boca Raton, FL, 2016), Chap. 9.
[32] A. Dequidt, D. R. Long, P. Sotta, and O. Sanseau, Mechanical properties of thin confined polymer films close to the glass transition in the linear regime of deformation: Theory and simulations, Eur. Phys. J. E **35**, 61 (2012).
[33] R. Masurel, S. Cantournet, A. Dequidt, D. Long, H. Montes, and F. Lequeux, Linear Viscoelasticity of polymer in their glass transition domains: 2d finite elements simulations, Macromolecules **48**, 6690 (2015).
[34] S. Kawana and R. A. L. Jones, Character of the glass transition in thin supported polymer films, Phys. Rev. E **63**, 021501 (2001).
[35] J. E. Pye and C. B. Roth, Two Simultaneous Mechanisms Causing Glass Transition Temperature Reductions in High Molecular Weight Freestanding Polymer Films as Measured by Transmission Ellipsometry, Phys. Rev. Lett. **107**, 235701 (2011).
[36] S. Merabia and D. Long, Heterogeneous dynamics and pressure dependence of the dynamics in van der Waals liquids, Macromolecules **41**, 3284 (2008).
[37] L. Conca, A. Dequidt, P. Sotta, and D. R. Long, Acceleration and homogenization of the dynamics during plastic deformation, Macromolecules **50**, 9456 (2017).
[38] G. Adam and J. H. Gibbs, On temperature dependence of cooperative relaxation properties in glass-forming liquids, J. Chem. Phys. **43**, 139 (1965).
[39] J. P. Garrahan and D. Chander, Geometrical Explanation and Scaling of Dynamical Heterogeneities in Glass Forming Systems, Phys. Rev. Lett. **89**, 035704 (2002).
[40] F. Ritort and P. Sollich, Glassy dynamics of kinetically constrained models, Adv. Phys. **52**, 219 (2003).
[41] A. J. Kovacs, La contraction isotherme du volume des polymères amorphes, J. Polym. Sci **30**, 131 (1958).
[42] J. Berriot, H. Montes, F. Lequeux, D. Long, and P. Sotta, Gradient of glass transition temperature in filled elastomers, Europhys. Lett. **64**, 50 (2003).
[43] D. J. A. Senden, J. A. W. Van Dommelen, and L. E. Govaert, Strain hardening and its relation to bauchinger effets in oriented polymers, J. Polym. Sci., Polym. Chem. Ed. **48**, 1483 (2010).
[44] Y. Fan, T. Iwashita, and T. Egami, How thermally activated deformation starts in mettalic glass, Nat. Commun. **5**, 5083 (2014).
[45] Y. Fan, T. Iwashita, and T. Egami, Energy lanscape-driven non-equilibrium evolution of inherent structure in disordered material, Nat. Commun. **8**, 15417 (2016).
[46] S. Merabia, P. Sotta, and D. Long, Heterogeneous nature of the dynamics and glass transition in thin polymer films, Eur. Phys. J. E **15**, 189 (2004).
[47] D. J. Plazek, V. Tan, and V. M. O'Rourke, Creep Behavior of ideally atactic and commercial polymethylmethacrylate, Abstracts of Papers of the American Chemical Society (1972), p. 2.
[48] C. E. Maloney and D. J. Lacks, Energy barrier scalings in driven systems, Phys. Rev. E **73**, 061106 (2006).
[49] L. Monnerie, J. L. Halary, and H. H. Kausch, Deformation, yield and fracture of amorphous polymers: Relation to the secondary transitions, *Intrinsic Molecular Mobility and Toughness of Polymers I*, Advances in Polymer Science Vol. 187 (Springer-Verlag, Berlin, Heidelberg, 2005), pp. 215–364.