Comment on "Relaxation Kinetics of Nanoscale Indents in a Polymer Glass"

Structural relaxation of amorphous materials is usually described as resulting from the contribution of microscopic transitions covering a spectrum of activation energies, $g(E)$ [1,2]. When $g(E)$ is flat, the relaxation kinetics follows a $\log(t)$ dependence [2,3]. Thus, it is quite surprising that Knoll *et al.* [4] do not rely on this classic model to describe their experimental results. Their model, relating the activation energy to the relaxation degree, is very appealing. However, their good fitting to experiment, with Σ_0 depending on the annealing temperature, cannot be an argument for the model validity because (a) before annealing the state is always the same and (b) the number of free parameters is too high to deliver meaningful values [5].

First, let us show that the experimental points can be fitted to the classical model [1,2]. According to it, a particular state d/d_0 is reached when the transitions with a given activation energy $E(d/d_0)$ take place, i.e., at time $t \approx \nu_0^{-1} \exp[E(d/d_0)/kT]$, where ν_0 is the attempt frequency [1]. For $d/d_0 = 0.6$, we obtain 2.0 eV and $\nu_0 \approx 2 \times 10^{23}$ s^{-1} for $t = 120$, 100, and 80 °C (inset of Fig. 1) [6]. Furthermore, the observed logarithmic dependence of d/d_0 on time is consistent with a flat spectrum between $E_{\min}$ and $E_{\max}$. We can thus fit the experimental points to the theoretical dependence [2,3]:

$$(d/d_0)(t) = (E_{\max} - E_{\min})^{-1} \int_{E_{\min}}^{E_{\max}} \exp[-t/\tau(E)]dE,$$
(1)

where $\tau(E) \equiv \nu_0^{-1} \exp(E/kT)$. An excellent fit is obtained with $E_{\min} = 1.87$, $E_{\max} = 2.54$ eV, and $\nu_0 = 2 \times 10^{24}$ s^{-1} (Fig. 1).

Second, as commented above, a necessary condition for the reliability of Knoll's model is its ability to fit the experimental points with a single set of parameters (E_a, Σ_0, and $\nu_0\Delta_\Sigma$). Here, we show that this condition is fulfilled. In the logarithmic regime, the time needed to reach a given $(d/d_0)/T$ value is thermally activated according to $t/T \propto \exp(E_a/kT)$. Application of this equation to the experimental points delivers $E_a = 2.54 \pm 0.19$ eV (inset of Fig. 1). Then, the slopes are consistent with $\Sigma_0 = 0.27$ and, finally, fitting the experimental points to Knoll's formula (Fig. 1) delivers $\nu_0\Delta_\Sigma = 5 \times 10^{22}$ s^{-1}.

In light of Fig. 1, we cannot decide which microscopic mechanism governs the structural relaxation. However, a formal aspect of Knoll's model could invalidate it. Knoll *et al.* consider that, during indentation, a number of chain segments become frozen in a state of higher energy [7]. During annealing, these segments rotate towards a lower energy state. The number of transitions per unit time that approach the material to equilibrium (n^-) should be proportional to or, at least, should increase with the number of segments in this "excited" state $N_{\rm exc}$. Since the relaxed state would be reached when most of these segments would
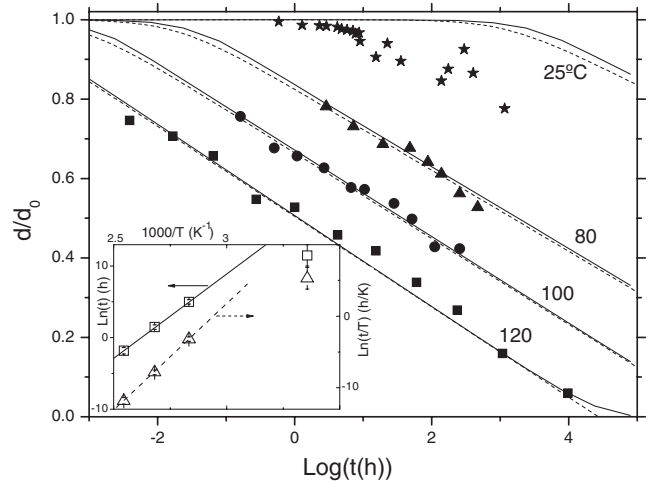

FIG. 1. Fit to the model of Gibbs (solid lines) and to that of Knoll (dashed lines). Inset: Activation energy at $(d/d_0) = 0.6$ for the Gibbs model (squares) and at $(d/d_0)/T = 2 \times 10^{-3}$ K^{-1} for Knoll's model (triangles).

have undergone this transition, we deduce that *the preexponential term* appearing in n^- should diminish as relaxation proceeds. It is very difficult to sustain that the relaxation rate ($d\Sigma/dt$) does not show any dependence on Σ in its preexponential term [Knoll's Eq. (1)]. In other words, the kinetics of the microscopic processes involved in structural relaxation cannot be of the zeroth order, as proposed by Knoll *et al.*

To conclude, we think that, unless a better justification is given for the model proposed by Knoll *et al.*, we should consider that their experimental results constitute an excellent example for the classical model of structural relaxation.

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[5] See EPAPS Document No. E-PRLTAO-103-065938 where we show that good fitting is achieved with an E_a value far from that quoted by Knoll *et al.* [4]. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
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