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Comment on "Temperature divergence of the dynamics of a poly(vinyl acetate) glass: Dielectric vs. mechanical behaviors" [J. Chem. Phys. 136, 154901 (2012)]

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The temperature dependence of polymer dynamics below the standard glass transition temperature T_g is of considerable interest.[1,2] For a better understanding of physical aging and the glass transition phenomenology, it is important to assess the temperature at which the relaxation times will tend to diverge, in particular whether this will occur near T_g or not until $T = 0$.[3] An inherent problem in obtaining relaxation time data below the calorimetric glass transition is the prohibitively long time required to attain equilibrium and to measure such a correlation decay. In a recent paper, Zhao and McKenna have addressed this issue and measured the equilibrium dynamics of poly(vinyl acetate) (PVAc) in the range from $T_g - 15$ K to $T_g + 30$ K,[4] using Struik's protocol[5] to determine that physical aging had been completed prior to recording the dielectric retardation, $\varepsilon(t)$, at the target temperature. The resulting shift factors, a_T, display a transition to a lower apparent activation energy near $T < T_g - 10$ K, where $\log_{10}(a_T)$ exceeds 2.5. Figure 9 of the paper by Zhao and McKenna[4] is declared as a comparison of their results with dielectric relaxation ($M = 1/\varepsilon$) data from time domain dielectric modulus experiments by Wagner and Richert,[6] but the dielectric retardation (ε) data set from that work is shown instead, which is limited to $T > T_g$. This erroneous comparison is reproduced in Fig. 1(a) and could suggest that previous dielectric experiments aimed at measuring very long quasi-equilibrium time constants have not been able to observe responses below $T_g - 10$ K for PVAc and thus missed this transition to a more Arrhenius like behavior.

Time domain measurements of the electric field relaxation at constant charge are an alternative approach to recording dielectric polarization.[7] For polar materials, this relaxation of the electric modulus, $M(t)$, decays faster than the retardation counterpart, $\varepsilon(t)$. Even for dispersive processes, the conversion from relaxation to retardation time constants is a purely mathematical procedure, and measuring $M = 1/\varepsilon$ instead of ε itself can thus reduce the time needed to determine the dielectric response below T_g considerably.[8] This $M(t)$ technique has generated average dielectric retardation times in excess of 1 yr for PVAc,[6] and an extended data set spanning the range from 3.1×10^{-9} s to 3.4×10^7 s in terms of the average retardation time constant has been tabulated in a later publication.[9] Figure 1(b) displays

the corrected version of comparing Zhao and McKenna's retardation data (squares)[4] with the relaxation experiments of Wagner and Richert (full circles),[6] including the retardation experiments that extend the shift factors for the same sample to higher temperatures (open circles).[9] This graph demonstrates that the dielectric relaxation data cited by Zhao and McKenna does reach shift factors up to $\log_{10}(a_T) = 5.5$, with no indication of a transition towards more Arrhenius like behavior.[10] In fact, the full data set that covers 16 decades in a_T is quite well described by a single Vogel-Fulcher-Tammann (VFT) curve,

$$\log_{10}(a_T) = A + \frac{B}{T - T_0}, \qquad (1)$$

with $A = -14.0$, $B = 727.9$ K, $T_0 = 250.3$ K ($T_g = 302$ K). Apart from the short time behavior,[11] the $M(t)$ decay curves related to these PVAc data are well represented by Kohlrausch-Williams-Watts (KWW)[12] type decays, $\exp[-(t/\tau)^\beta]$, with a stretching exponent $\beta = 0.4$ that shows little variation with temperature.[6] The difference in T_g values for the two PVAc samples is likely to originate from the different molecular weights, $M_W = 157$ kg/mol versus $M_W = 14.5$ kg/mol, for the Zhao[4] and Wagner[6] samples, respectively.

While the shift factors for the segmental motion in Fig. 1(b) agree for $T > T_g$, a considerable deviation sets in for $T < T_g - 5$ K. A source of uncertainty in Zhao's data set is the time limitation of the dielectric retardation experiment, with $\varepsilon(t)$ in Fig. 7 of Ref. 4 being restricted to $t \leq 100$ s. For temperatures $T < T_g - 10$ K, the $\varepsilon(t)$ experiment thus captures only an initial small part of the correlation decay, where time-temperature superposition may fail and the KWW fit is no longer satisfactory.[11] For a quantitative illustration, it is noted that the KWW fit to $\varepsilon(t)$ resulted in $\tau = 4.53$ s and $\beta = 0.52$ at the reference temperature of 308.3 K.[4] The longest shift factor for $\varepsilon(t)$ observed by Zhao and McKenna is $a_T \approx 10^{4.7}$, implying that the KWW time constant is $\tau \approx 2 \times 10^5$ s at $T = T_g - 15.8$ K. With an experimental window of $t \leq 100$ s, the observation in this case is limited to the top 2% of the decay, $1 - \exp[-(t/\tau)^\beta] = 0.02$, with $t/\tau = 100$ s$/2 \times 10^5$ s $= 5 \times 10^{-4}$ and $\beta = 0.52$. In the case of the $M(t)$ data, all shift factors for $T < T_g$ are based upon the steepest segments of the $M(t)$
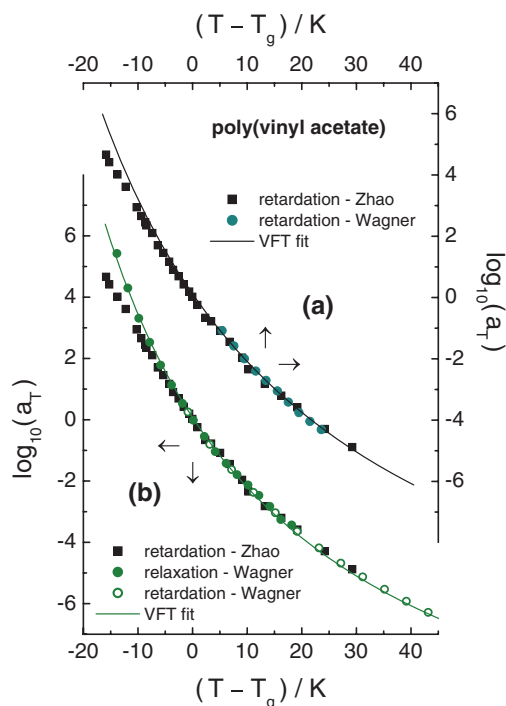
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FIG. 1. Black squares in panels (a) and (b) represent the dielectric retardation shift factors, a_T, versus reduced temperature, $T - T_g$ ($T_g = 308.3$ K) for PVAc reproduced by careful digitization from Fig. 9 of Ref. 4. (a) Blue dots represent dielectric retardation results from Wagner and Richert (Ref. 6), which are designated as "dielectric relaxation" results in the original figure in Ref. 4. The line is a VFT fit to data above T_g. (b) Green full circles represent the true dielectric relaxation results from Wagner and Richert (Ref. 6), green open circles are for dielectric retardation results of the same sample, see Ref. 9. The line is a VFT fit to the entire PVAc data set (green symbols) that ranges from 3.1×10^{-9} s to 3.4×10^7 s in terms of the average retardation time constant (Ref. 9).

versus lg$t$ decay, i.e., where $t \approx \tau$, via KWW fits.[6] It should be noted that the raw $M(t)$ data shown in the original publication will not display time-temperature superposition at very long times due to an additional exponential long time decay of the field that is intrinsic in the experimental setup. The KWW fits to the $M(t)$ data account for this effect, but the data curves were not corrected.[6]

In conclusion, a crossover to a more Arrhenius like activation behavior and a strong decoupling of dielectric and mechanical modes may not be general features of the equilibrium dynamics of poly(vinyl acetate) below the calorimetric glass transition. Observing VFT behavior for dielectric retardation times reaching $\tau > 1$ yr still does not imply the dynamic arrest of the system at a finite temperature.

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