Comment on "Merging of α and slow β relaxation in supercooled liquids"

R. Bergman* and C. Svanberg

Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden
(Received 7 January 2005; revised manuscript received 15 June 2005; published 20 October 2005)

Fujima [T. Fujima, H. Frusawa, and K. Ito, Phys. Rev. E **66**, 031503 (2002)] report on broadband dielectric relaxation measurements on two glass-formers. They find that the relaxation times of the β relaxation follow different temperature dependences above and below the glass-transition temperature, T_g; i.e., there appears to be a crossover at T_g where the activation energy of the β relaxation change. In this Comment we show that the observed behavior can be explained by analyzing the merging of the α and β relaxations using an approach proposed by Williams. This analysis clearly shows that the low temperature (below T_g) behaviors of the α and β relaxations can be used to describe also the high-temperature behavior (above T_g). The apparent change in activation energy is thus not to be identified with a change in relaxation mechanism.

I. INTRODUCTION

The main feature of glassy dynamics is the rapid slowing down of the main (α) relaxation process when temperature is lowered towards T_g. Explaining the non-Arrhenius and non-Debye nature of this process remains an outstanding challenge in physics. The faster and normally weaker β relaxations are less temperature sensitive than the α relaxations and are generally found to have an Arrhenius temperature dependence. As stated in Ref. [1] recent research in the field focuses its attention to the temperature T_{ex} where, along with other changes in experimental observables, the extrapolated Arrhenius temperature dependence of the β-relaxation time intersects the non-Arrhenius temperature dependence of the α-relaxation time. It is also found that T_{ex} and the accompanying anomalies occur in the vicinity of the critical temperature of the mode coupling theory. Thus, studies of the dynamics in the merging region are therefore important for an advancement of a deeper understanding of the glass transition [2–5].

In Ref. [1] Fujima *et al.* perform broadband dielectric relaxation measurements on two glass-formers with unusually strong β relaxations in order to follow the dynamics in the merging region. The systems, Sorbitol and m-fluoroaniline, have been studied before but in those studies the β relaxations were not followed to as high temperatures as in Ref. [1]. The excellent data presented clearly show the presence of a secondary relaxation also at temperatures higher than T_{ex}. This implies that the α and β relaxation do not merge at T_{ex} in contrast to what could be expected from a straightforward extrapolation of the low-temperature behaviors of the relaxation times. In Ref. [1] this is explained by a change of the activation energy of the β relaxation at a temperature just below T_{ex}. Indeed, this change seems to be obvious in the Arrhenius plots for both systems. However, in Ref. [1] the total dielectric loss spectra are described using a superposition of two peaks which is valid only if the two processes are separated in time or space. Below T_g these

criteria are fulfilled as the relaxation times of the α and β relaxations are separated with more than eight decades. Above T_g, however, the time scales of the α and β relaxations rapidly become more and more similar and a simple superposition is no longer valid. An attempt to include the basic feature of the resulting total correlation function of multiple relaxation processes has been given by Williams [6]. In a simplified approach the processes are assumed to be statistically independent, which certainly is an oversimplification but results in a convolution of the processes which is definitely more correct than a pure superposition. The resulting simplified ansatz [6] has been shown to successfully explain the observed dynamics in the merging region in many glass-formers [7–9].

In this Comment we reanalyze the relaxation time data in Ref. [1] and provide an alternate explanation for the observed change of activation energy of the β relaxation. We show that if the data is analyzed according to Williams' ansatz, the observed behavior can be explained without invoking any change in the underlying β-relaxation mechanism.

II. ANALYSIS

According to Williams' ansatz the total normalized relaxation function in the time domain is given by

$$\phi(t) = a\phi_\alpha(t) + (1 - a)\phi_\alpha(t)\phi_\beta(t). \qquad (1)$$

Here $\phi_\alpha(t)$ and $\phi_\beta(t)$ are the normalized relaxation functions for the α and β relaxation processes, respectively, and a is the relative strength of the α process. A key issue is that the product $\phi_\alpha(t)\phi_\beta(t)$ constitutes an effective β relaxation $\phi_{\beta\text{eff}}(t)$. This infers that the corresponding permittivity for the effective β relaxation, $\varepsilon^*_{\beta\text{eff}}(f)$, is a complex convolution of $\varepsilon^*_\alpha(f)$ and $\varepsilon^*_\beta(f)$. In this paper the effective β relaxation in the merging region was calculated as described in Ref. [10]. An original β relaxation was reconstructed using the extrapolation of relaxation times below T_g, where the α and β relaxations are well separated and the superposition ansatz valid. Here we used the literature data for the β relaxation time [11] referred to in Ref. [1] and the temperature depen-
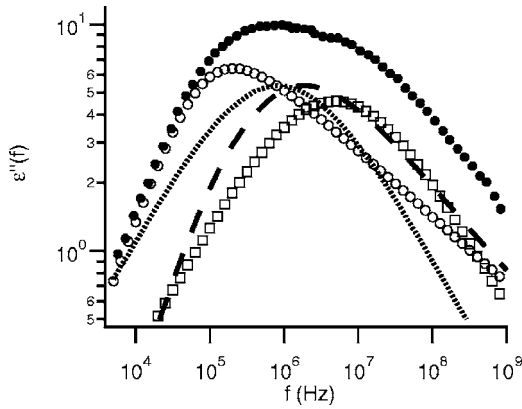
*Electronic address: f5xrb@fy.chalmers.se

FIG. 1. The original experimental data [1] (filled circles) and its components from superposition and Williams analysis at T =310 K. The α relaxation (circles) is identical for the two types of analysis while the superposition β processes (squares) differs from the extrapolated low temperature β relaxation (dotted line) which is used for calculating the effective β relaxation (dashed line).

dence of the shape parameter given in Fig. 4(b) of Ref. [1]. Since the α relaxation is identical in the Williams' ansatz and the superposition analysis, the shape and temperature dependence of the α relaxation was directly extracted from the presented data in Ref. [1]. In this manner we have reconstructed the loss peaks for the α and extrapolated β relaxations. These peaks are then used to calculate the effective β relaxation in the merging region above T_g. The reconstructed and calculated peaks at $T=310$ K, which is close to T_{ex} =312±4 K, are compared with the reported β relaxation in Fig. 1. The figure shows that the effective β is significantly faster than the underlying β relaxation which is extrapolated from below T_g. However, importantly, the peak position of the effective β loss peak almost coincides with the reported [1] β loss peak from the superposition analysis. Also note that the effective β process is not symmetric.

In Fig. 2 we show the peak relaxation time for the obtained effective β relaxation together with the reported data [1] in the merging region. It is clearly shown that the relax-
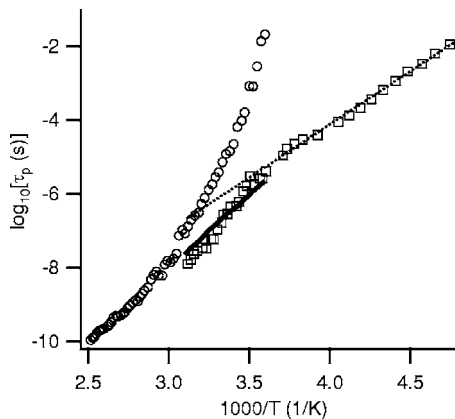

FIG. 2. Relaxation times of Sorbitol in the merging region. The relaxation times of the generated effective β relaxation are shown as a full line. The α (circles) and extrapolated low temperature β (dotted line) relaxation are shown together with the superposition β (squares) relaxation as reported in Ref. [1].

ation times of the effective β relaxation coincides with the relaxation times reported in Ref. [1]. Analyzing the Sorbitol data according to Williams' ansatz thus gives an effective β-relaxation peak also above $T=T_{ex}$ contrary to what can be expected from a straightforward extrapolation from low temperatures of the β relaxation time. The change of slope in the Arrhenius plot can thus be explained without having to address any change in the temperature dependence of the β relaxation.

III. DISCUSSION

The results of the alternate analysis for Sorbitol presented in the previous section are completely analogous to what has been reported for several polymers [8,9]. Only a few low molecular weight glass-formers [7] has been subject to a Williams' ansatz analysis and therefore the broadband high quality data of [1] are extremely important for a confirmation of the general validity of Williams' ansatz. From these studies on very different glass-formers it is clear that by analyzing relaxational data in the merging region using Williams' ansatz a wide spectra of merging scenarios can be explained. Indeed, when considering the range of shapes and temperature dependences of α and β relaxations, resulting relaxation times of the effective β relaxations may differ from the ones of the underlying β relaxations in various degrees. In particular, the temperature where $\tau_{\beta\mathrm{eff}}$ starts deviating from τ_β will be intimately connected to the width of the relaxation processes as shown in [8].

In general, for many materials, observed changes in the temperature dependence of the β-relaxation time can thus be explained by the convolution of the α and β relaxations forming an effective β relaxation. The dynamical features of this effective β relaxation is identical to the β relaxation below T_g, but becomes increasingly affected by the α process, as temperature increases, causing an apparent change in the activation energy. Furthermore, also the shape of the effective β relaxation changes in the merging region. Typically it transforms continuously from a symmetric to an asymmetric shape when temperature is increased and the effective β relaxation becomes increasingly affected by the α relaxation. Of course, this change in shape will not be seen directly in experimental data as the low-frequency part of the peak will coincide with more and more of the α peak.

IV. CONCLUSION

We have shown that the observed change in activation energy above T_g for the effective β relaxation in Sorbitol can be explained by analyzing the relaxation data according to Williams' ansatz. The result is completely analogous to what has been reported for the merging region of several other glass-formers, mainly polymers, and thus confirms the general validity of Williams' product ansatz. The apparent change in activation energy, in the present and other systems, should thus not be identified with a change in relaxation mechanism for the underlying β relaxation.

[1] T. Fujima, H. Frusawa, and K. Ito, Phys. Rev. E **66**, 031503 (2002).

[2] E. Rössler, Phys. Rev. Lett. **65**, 1595 (1990).

[3] F. Garwe, A. Schönhals, H. Lockwenz, M. Beiner, K. Schröter, and E. Donth, Macromolecules **29**, 247 (1996).

[4] M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13200 (1996).

[5] J. Mattsson, R. Bergman, P. Jacobsson, and L. Börjesson, Phys. Rev. Lett. **94**, 165701 (2005).

[6] G. Williams, Adv. Polym. Sci. **33**, 60 (1979).

[7] F. Alvarez, A. Hoffman, A. Alegria, and J. Colmenero, J. Chem. Phys. **105**, 432 (1996).

[8] R. Bergman, F. Alvarez, A. Alegria, and J. Colmenero, J. Chem. Phys. **109**, 7546 (1998).

[9] D. Gomez, A. Alegría, A. Arbe, and J. Colmenero, Macromolecules **34**, 503 (2001).

[10] C. Svanberg, R. Bergman, and P. Jacobsson, Europhys. Lett. **64**, 358 (2003).

[11] H. Wagner and R. Richert, J. Phys. Chem. B **103**, 4071 (1999).