

Reply to “Comment on ‘Merging of the α and β relaxations in polybutadiene: A neutron spin echo and dielectric study’”

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(Received 18 May 1998; revised manuscript received 3 March 1999)

In their Comment [E. Donth, K. Schroter, and S. Kahle, preceding Comment, Phys. Rev. E **69**, 1099 (1999)] on our paper [A. Arbe, D. Richter, J. Colmenero, and B. Farago, Phys. Rev. E **54**, 3853 (1996)], Donth *et al.* conclude that the procedure followed by us for analyzing data of glass-forming polymers, which is based on a Williams-like ansatz, is not suited for the merging region of the α and β dielectric processes. They claim that a simple addition ansatz is the correct procedure. In this Reply, by considering new dielectric data of six different polymers, we show that our procedure seems to be certainly suitable for describing the merging region without any *ad hoc* assumption. Moreover, we also show that an unbiased application of the addition ansatz in fact gives support to the procedure followed by us. [S1063-651X(99)03007-X]

PACS number(s): 64.70.Pf, 61.12.Ex, 61.41.+e

In a recent paper [1], we investigated the merging of the α and β relaxation processes in polybutadiene (PB), a well known glass-forming polymer, by means of the combination of two very different experimental techniques: neutron spin echo (NSE) and broadband dielectric spectroscopy (DS). First of all, we would like to emphasize that the correlators observed by these two techniques are rather different. NSE measures the normalized density-density correlation function, i.e., $S(Q,t)/S(Q,0)$, where $S(Q,t)$ is the dynamic structure factor (Q is the momentum transfer). This observable provides direct space-time information about the actual microscopic relaxation processes. DS, on the other hand observes the frequency-dependent complex dielectric permittivity $\epsilon^*(\omega)$, which reflects the orientational dynamics of the molecular dipoles in the sample.

Therefore, we should, in principle, expect different results when a given relaxation process is observed either directly by NSE or indirectly by DS. The results obtained by us for PB [1] by employing NSE and DS revealed some well known similarities (e.g. the same shape of the α relaxation is observed by NSE and DS), but also clear differences likely related to the different natures of the techniques used. However, the main conclusion of the paper was that both sets of measurements seem to mirror in a different way the same physics: the α and β processes can be considered in a good approximation as statistically independent processes.

Our approach was first of all to study the α - and β -relaxation processes by neutron scattering. There, the theoretical understanding of the response function is well developed and van Hove correlation functions may be strictly applied. These experiments revealed to our own astonishment that to a very good approximation the correlation functions related to α and β relaxation appear as a product, validating the assumption of statistically independent processes. If a

neutron experiment addressing the dynamics on a molecular level in space and time is very compatible with the statistical independence of both processes, then this observation must imply that such independence must be at the basis of an interpretation of results from other experimental techniques as well.

The problem now is how to express statistical independence in terms of a dielectric relaxation function. Donth *et al.* [Phys. Rev. E **60**, 1099 (1999)] point out that the time correlation function of a vector quantity such as the dipolar orientation might turn negative and therefore may not be interpreted as a van Hove correlation function, which measures probabilities. In principle, Donth *et al.* are correct. However, in the case of the orientational polarization processes of most condensed systems at frequencies lower than 10^{11} Hz, the step-response function [e.g., $\varphi(t)$ in Eq. (1) of Ref. [2]] can be built as a superposition of exponentials weighted by a given distribution of relaxation times (see, e.g., Chap. VIII of Ref. [3]). In the framework of the Kubo theory [3], this step-response function is equal to the autocorrelation function of the total macroscopic dipole moment, which thereby cannot be negative for orientational polarization processes. This is not the case for the induced polarization (atomic or electronic) processes, which take place at higher frequencies and which are not involved in the α and β relaxations. However, although under certain conditions the step-response function can also represent a microscopiclike correlation function (see, e.g., Chap. X of Ref. [3]), a direct molecular interpretation is extremely difficult. In order to be precise, the microscopic correlation function should also contain cross-correlation terms due to the specific interactions between molecular dipoles. Therefore, approximations are carried out regularly in order to arrive at a treatable description of experimental results. These models very often do

not carry the full complexity of the dielectric response but try to elucidate essential aspects of it. Williams' product ansatz [4] is such an approach which may directly be interpreted in terms of van Hove correlation functions for statistically independent processes. Therefore, after the neutron results on the dynamic structure factor, it was only natural to choose the ansatz of Williams and to investigate whether this approach [Eqs. (1) and (2) in Ref. [2]] allows for consistent data analysis.

As we have shown in Ref. [1], this is indeed the case. In this reply, we would like to further prove this concept and apply the convolution approach of Williams to dielectric data from a number of different polymers that display dielectric traces similar to the different scenarios of Donth *et al.* (Ref. 5 of Ref. [2]). In addition, we also take the point of view of Donth *et al.* and evaluate the same data in terms of the addition approach [Eq. (4) of Ref. [2]] and compare the corresponding characteristic times. In this way, we show that in each case for the correlation function of the “*b*” or “*a*” process, $\varphi_{b/a} = \varphi_\alpha \varphi_\beta$ holds, where φ_α and φ_β describe the extrapolated low-temperature α and β processes. There is no need to invoke additional phenomena around the merging regime; the whole set of phenomena emerge naturally without any further assumption on the basis of the low- T processes.

In order to investigate the different dielectric scenarios, we have recently carried out a complete set of new dielectric measurements with different glass-forming polymers, covering a broad frequency range that extends from 10^{-2} to 10^9 Hz. The systems investigated are poly(epichlorhydrin) (PECH), poly(2-hydroxypropyl ether bisphenol A) (PH), poly(ethyl acrylate) (PEA), tetramethyl bisphenol polycarbonate (TMPC), poly(vinyl acetate) (PVAc), and poly(methyl methacrylate) (PMMA). These are polymers with very different chemical structure, dipole moment, T_g , and ratio between the strength of the α and β relaxations at $T \sim T_g$ [Eq. (4) of Ref. [2]]. The experimental results have been alternatively analyzed by means of the addition ansatz or by the product approach [Eqs. (1) and (2) of Ref. [2]]. The complete results obtained are planned to be published in a future paper [5] in which the uncertainties involved in the fitting procedure by both concepts will be discussed. The results corresponding to PMMA have already been published [6].

Figure 1 displays the results of the two different analyses. The solid lines present the traces of τ_α , the characteristic time of the α process; the dashed line displays the extrapolated low- T β process. The uncertainty of the slope is very small, since we have covered a wide T range below T_g . The open circles result from the evaluation in terms of the addition approach $\tau_{b/a}$ (*a, b* process), while the crosses were obtained applying the convolution concept on the basis of the extrapolated low T processes and represent $\tau_{\beta \text{ eff}}$, the relaxation time corresponding to $\varphi_{\beta \text{ eff}}(t)$ [Eq. (2) of Ref. [2]].

The most relevant feature shown in Fig. 1 is that for all polymers $\tau_b(T)$ is always equivalent to $\tau_{\beta \text{ eff}}(T)$.

(i) As was expected, at $T \leq T_g$ it is clear that both $\tau_b(T)$ and $\tau_{\beta \text{ eff}}(T)$ tend to the Arrhenius behavior shown by $\tau_\beta(T)$.

(ii) When the α and β processes remain well separated even at $T > T_g$, i.e., there is no actual merging in the experi-

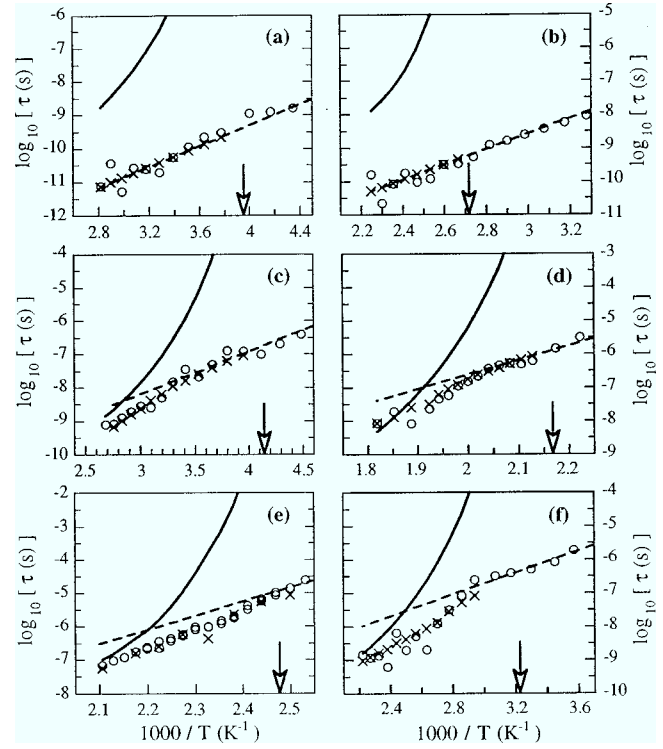


FIG. 1. Temperature dependence of the characteristic times of (a) PEA, (b) PH, (c) PECH, (d) TMPC, (e) PMMA, and (f) PVAc. Solid lines correspond to the α relaxation time $\tau_\alpha(T)$, dashed lines to the extrapolation of the β relaxation $\tau_\beta(T)$ ($T < T_g$), circles to the *b* process $\tau_b(T)$, and crosses to $\tau_{\beta \text{ eff}}(T)$. See text for the definition of these relaxation times. The arrows mark the corresponding T_g 's.

mental window (see PEA and PH), both $\tau_b(T)$ and $\tau_{\beta \text{ eff}}(T)$ follow the extrapolated Arrhenius behavior of $\tau_\beta(T)$ at $T > T_g$.

(iii) When the two processes overlap in the experimental T window, both $\tau_b(T)$ and $\tau_{\beta \text{ eff}}(T)$ continuously deviate, but in the same way, from the extrapolated $\tau_\beta(T)$ behavior.

The equivalence between τ_b and $\tau_{\beta \text{ eff}}$ implies that the results of the “well accepted” addition ansatz naturally evolve from the simplified Williams ansatz. It is noteworthy that the equivalence directly emerges from the experimental results corresponding to very different systems and not from any particular interpretation of the data. Our finding leads to the following consequences.

(i) To a good approximation, the phenomenological functions $\varphi_\alpha(t)$ and $\varphi_\beta(t)$ may be interpreted as molecular dipolar van Hove-type correlation functions corresponding to two statistical independent processes. This result is in complete agreement with the impact of the NSE technique on the structural α and β processes, although it is clear that $\varphi_\alpha(t)$ and $\varphi_\beta(t)$ are different correlators than the dynamic structure factors $S_\alpha(Q, t)$ and $S_\beta(Q, t)$ measured by NSE.

(ii) The dielectric results in the merging region $T > T_g$ of many different systems (“different scenarios” of Donth *et al.*) are very well explained in terms of the results obtained in the temperature region below and around T_g , where the α and β dielectric processes are well separated. This result is by no means trivial and shows that it is not necessary to invoke any additional assumption (e.g., the onset of any co-

operativity). It is worth emphasizing that the “economy of assumptions” has always been considered as a paradigm in science.

(iii) The deviations of $\tau_b(T)$ and $\tau_{\beta \text{ eff}}(T)$ from the low-temperature Arrhenius behavior of $\tau_\beta(T)$ as the temperature increases is not related to any particular change of relaxation mechanism, but to overlap effects between α and β processes. Therefore, the so-called a process by Donth *et al.*, which corresponds to the b process at $T > T_{\text{on}}$ can be explained in terms of the low-temperature α and β processes alone, thereby connecting both temperature regions.

In summary, we have shown that an application of Williams’ convolution approach to the evaluation of dielectric spectra in the merging regime of the α and β processes leads to a natural explanation of the observed deviations of the β trace from the low- T Arrhenius behavior and agrees perfectly with what is obtained from the conventional addition ansatz.

Therefore, it seems that the controversy between the addition ansatz and the Williams convolution ansatz invoked by Donth *et al.* is an artificial problem. In our opinion, the problem of the analysis carried out by Donth *et al.* is that, in

fact, they are applying not an unbiased addition ansatz, but what they call the “splitting ansatz.” This approach involves an *ad hoc* assumption about a discontinuity of the relaxation mechanism at T_{on} and the onset of the cooperativity of the α relaxation. This assumption is mainly based on the result $f_\alpha = 0$ at T_{on} , which naturally evolves from the convolution approach, where, with increasing temperature, an increasing fraction of the dipolar orientation is relaxed by $\varphi_{\beta \text{ eff}}$ alone.

In contrast, our analysis has shown that (i) the addition and the convolution ansatz both lead to consistent results; (ii) the convolution approach provides a natural explanation for the temperature dependence of the dielectric response in the merging regime on the basis of the low- T data without invoking any new mechanism; and (iii) finally, though dielectric spectroscopy and NSE do not probe the same correlation functions, the underlying physical principle of statistically independent processes characterizes the response function in a similar way.

We acknowledge Professor A. Alegría for helpful discussions.

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