

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

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The evaluation method of dielectric data based on a Williams product ansatz [A. Arbe, D. Richter, J. Colmenero, and B. Farago, *Phys. Rev. E* **54**, 3853 (1996)] is not suited to the crossover region of the dynamic glass transition. This method is insensitive to the shape, position, or even existence of at least one of the relaxation functions if, in the extrapolation from below to above the crossover region, the two processes cross or approach one another. Since a crossover region without any particular change in the relaxation mechanism of these processes can in fact be adjusted by this method, better dielectric data for polybutadiene in the gigahertz frequency region are needed to determine whether or not there are peculiarities in the dielectric function. It would be an odd assumption that the many particularities in the crossover region in other instances are not reflected in the dielectric response. [S1063-651X(99)02607-0]

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I. INTRODUCTION

In the relaxation chart of amorphous polymers, the main transition α usually approaches the local β process [1] in the so-called crossover region. The study of this region by inelastic neutron scattering documented in the paper by Arbe *et al.* [2] was completed by dielectric response. In that study, data evaluation was correlated with the statistical independence of α and β , similarly to that used for the scattering evaluation, and was therefore based on the Williams product ansatz [3].

Working with this ansatz in the crossover region seems dangerous for two reasons.

(i) A product of two correlation functions, $\varphi_{12}(t) = \varphi_1(t)\varphi_2(t)$, forces merging to a new correlation function above the crossover, $\varphi_a(t)$, with the property that the new correlation time τ_a corresponds approximately to the shorter correlation time, $\tau_a \approx \min\{\tau_1, \tau_2\} = \tau_1$, say. In the extreme extrapolation case, $\tau_2 \gg \tau_1$, the transition region of φ_2 is completely quenched by $\varphi_1 \approx 0$ for $\tau_1 \ll t \approx \tau_2$, whatever the shape of φ_2 may be. This insensitivity allows, within certain limits, an arbitrary treatment of the slower relaxation φ_2 above the crossover, if the experimental data in this (high-frequency) region are of moderate accuracy.

(ii) The dielectric study of Arbe *et al.* [2] further shows that an extrapolation of both processes from below the crossover, where they are well separated, to above the crossover is possible without any particularity in this region, namely, without qualitative changes in the relaxation processes. This also seems dangerous since, as a rule, many particularities are observed there; cf. the recent review of Sokolov [4]. An alternative evaluation of dielectric data [5] would also show particularities.

The paper is organized as follows. In Sec. II, the dielectric evaluation method of Arbe *et al.* is briefly recapitulated. In Sec. III our starting point is described in more detail. Section IV is a brief discussion of the two conflicting points of view. We do not comment on the neutron scattering study of Arbe's paper, which is actually pioneering work.

II. THE DIELECTRIC MERGING APPROACH OF ARBE *et al.*

The evaluation method of Arbe *et al.* is first based on an additive formula,

$$\varphi(t) = f_\alpha \varphi_\alpha(t) + (1 - f_\alpha) \varphi_{\beta_{\text{eff}}}(t), \quad (1)$$

and then fed with a product ansatz [3] from underlying α and β processes,

$$\varphi_{\beta_{\text{eff}}}(t) = \varphi_\alpha(t) \varphi_\beta(t). \quad (2)$$

The relaxation functions $\varphi_i(t)$, $i = \alpha$ or β are defined by dielectric compliance, $\varepsilon(t) = \Delta \varepsilon \varphi(t)$. Both relaxation functions, $\varphi_\alpha(t)$ and $\varphi_\beta(t)$, correspond, via the fluctuation dissipation theorem (FDT), to autocorrelation functions of polarization fluctuations (dipole-dipole correlation), with the general property $|\varphi_i(t)| \leq \varphi_i(0) = 1$, $t \geq 0$. The relative strength factor for the α process, f_α , $0 \leq f_\alpha \leq 1$, is interpreted as the relative fraction of the polarization relaxed *only* by the α relaxation, i.e., with no β assistance.

A first extrapolation of α and $\beta = \beta_{\text{eff}}$ of Eq. (1) without the use of Eq. (2) [Fig. 1(c)] would result in an intersection of both α and β traces in the Arrhenius diagram (see their Fig. 11). The intersection temperature is called merging temperature T_M . This intersection is subsequently avoided by the product ansatz Eq. (2) for $\varphi_{\beta_{\text{eff}}}(t)$, since the product of two decaying functions always decays faster than each function of both (see their Fig. 13).

Extrapolation [Fig. 1(a)] to above the crossover ($T > T_M$) needs a definition of α or β because only one process is observed there. This is done by β extrapolations from low-temperature behavior, where α and β are well separated and, therefore, well defined. Arbe *et al.* used only f_α [Fig. 1(b)] and the relaxation time τ_{KWW} of the α relaxation as free fit parameters, without considering any particular change in the relaxation mechanism of these processes.

The main result is an Arrhenius-plot scenario [Fig. 1(a)] with a remaining gap of about 0.8 frequency decades be-

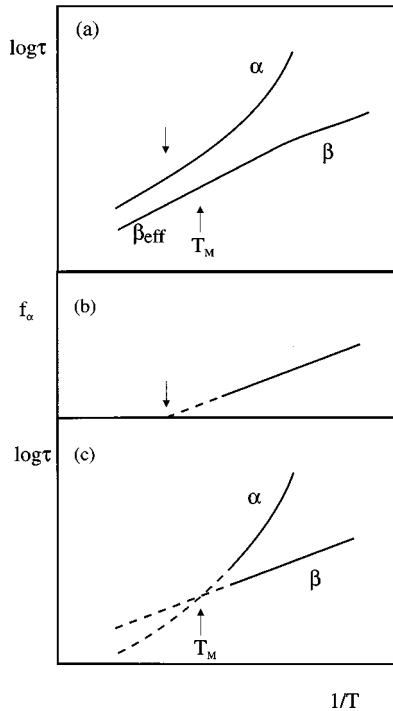


FIG. 1. Dielectric merging scenario according to Ref. [2]. (a) Traces in the Arrhenius diagram resulting from a phenomenological evaluation of dielectric data according to Eqs. (1) and (2). (b) Disappearance of the “only α ” relaxation strength f_α at \downarrow . (c) Intersection of the formally extrapolated “underlying” α and β traces in the Arrhenius diagram at the merging temperature T_M .

tween the α process and a continuous (with β) $\varphi_{\beta_{\text{eff}}}(t)$ process. The strength factor f_α tends almost linearly to zero (indicated by a down arrow \downarrow in Figs. 1(a) and 1(b)). Nevertheless, the α trace is continued to $T > T_\downarrow$.

III. OUR STARTING POINT

We start from the following statements.

(1) Neutron spin echo and dielectric experiments measure different correlation functions.

(2) Thus, an interpretation of the correlation function in terms of a probability and the concomitant “product” ansatz for statistically independent processes that may work for the density autocorrelation function measured in neutron scattering does not imply the same for the dipole-dipole autocorrelation function that is measured in dielectric spectroscopy. “It is therefore necessary, in general, to compare the time-correlation functions obtained from several related experiments in order to establish the mechanism of relaxation” [6].

(3) Extension of the precisely measurable low-temperature behavior of α and β processes to higher temperatures is biased in that it assumes that the relaxation mechanisms α and β do not change their physical nature in the crossover region.

(4) The term “statistical independence” is not given *a priori* but must be, according to Kolmogorov [7], deduced from the explanations and specifications of such conditions under which any data of real phenomena can be considered as statistically independent.

According to the FDT, as mentioned above, the relaxation

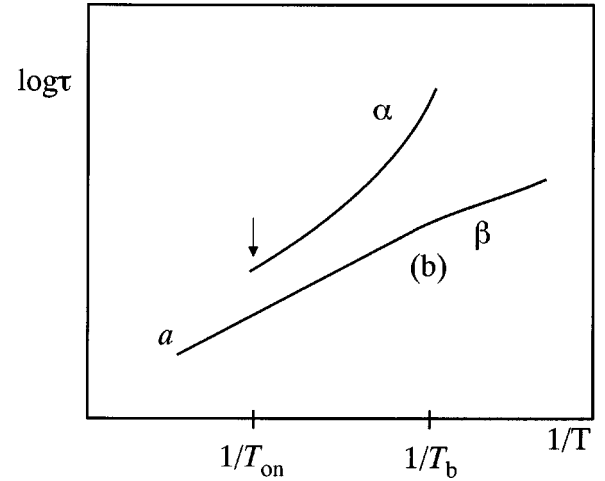


FIG. 2. Splitting scenario of Ref. [5]. The α process has a separate α onset \downarrow at T_{on} ; the a high-temperature process is continuously connected with the local β process by a crossover bend (b) at T_b [9].

functions $\varphi(t)$ are correlation functions. The general condition $|\varphi(t)| \leq \varphi(0) = 1$ does not exclude negative φ values ($\varphi < 0$). Since any probability density $p(x)$ of a random process $x(t)$ must be positive, $p(x) \geq 0$, in general $\varphi(t)$ cannot be interpreted as a (conditional) probability density. The interpretation of φ as a probability, and thus the interpretation of the product $\varphi_1 \varphi_2$ by statistical independence of two processes, $x_1(t)$ and $x_2(t)$, needs a model for the x variable that ensures $\varphi \geq 0$. Such models are described in the literature [8] and will be called “polarization decay models.” In principle, the dipole-dipole autocorrelation function φ stemming from a vector quantity may behave differently than a density-density autocorrelation function stemming from a scalar quantity without the possibilities of $\downarrow \uparrow$ vector compensation [9].

Less problematic would be an interpretation of the spectral density $G(\omega)$ [being a Fourier transform of $\varphi(t)$] as a probability density. Since $G(\omega) \geq 0$ (Khinchin theorem [10]), and since any fluctuation is based on probabilities, $G(\omega)$ can always be interpreted as the probability density of the entropy production in a $d \log \omega$ interval at ω , with ω the frequency. The Williams product ansatz Eq. (2), however, corresponds to a convolution of two $G(\omega)$ functions,

$$\varphi_1(t) \varphi_2(t) \Leftrightarrow G_1(\omega) * G_2(\omega). \quad (3)$$

The spectral interpretation [10] can then be based on a *sum* of two statistically independent stochastic functions, $x(\omega) = \xi_1(\omega) + \xi_2(\omega)$, defined here as a function of frequencies. Thus we arrive at a polarization model with two independent $x(\omega)$ components. Equation (3) seeks to represent an entropy production of a sum process $x(\omega)$ where the polarization can independently decay by 1 or 2, i.e., by ξ_1 or ξ_2 .

The “splitting” ansatz alternatively used in Ref. [5],

$$\begin{aligned} \varepsilon^* &= \varepsilon_\alpha^* + \varepsilon_\beta^* + \dots & \text{for } T < T_{\text{on}}, \\ \varepsilon^* &= \varepsilon_a^* + \dots & \text{for } T > T_{\text{on}}, \end{aligned} \quad (4)$$

where T_{on} is an onset temperature in the crossover (Fig. 2), corresponds to a sum of correlation functions or spectral den-

sities, $G(\omega) = G_1(\omega) + G_2(\omega)$. The entropy production results from either the 1 or the 2 relaxation, $\varphi_1(t)$ or $\varphi_2(t)$ (not from 1 or 2 dipoles), which are assumed to be statistically independent. Equation (4) is not biased toward the mutual arrangement of relaxation traces of an Arrhenius diagram. Formally, φ_{eff} of the product ansatz (2) corresponds to ε_β for $T \ll T_{\text{on}}$ and to ε_α for $T \gg T_{\text{on}}$. For shear relaxation, the use of additive compliances was addressed by Plazek [11].

IV. DISCUSSION

At first sight, Figs. 1(a) and 2 seem to be rather similar. The α relaxation intensity tends linearly to zero at onset in the crossover region, and there remains a gap of about one frequency decade between α and another trace that is a continuation of the β dispersion zone to higher temperatures. But the interpretation is different.

In the paper of Arbe *et al.*, the continuous high-temperature trace is labeled $\varphi_{\beta_{\text{eff}}}$. The corresponding distribution of relaxation times should “include the modifications of the β relaxation by the presence of the α relaxation.” Their conclusion for the merging region is that “the higher the temperature, the more similar becomes the shape of the distribution function of relaxation times of the effective β relaxation to the shape of the distribution function of relaxation times of the α relaxation, but shifted in the $\ln \tau$ axis” (see their Fig. 15 and the related discussion). This presents a puzzling situation in which a high-temperature relaxation β_{eff} is introduced as some kind of a modified β relaxation but realized as being dominated by α -like processes.

Alternatively [5], the high-temperature process can be considered as a distinct relaxation zone a , with no attempt to compose it from α and β , by statistical independence. The dielectric data of Arbe *et al.* may also be interpreted in this framework. Their finding of a more similar shape (“asymmetrization”) of the relaxation functions of α and a (their β_{eff}), the disappearance of the α strength factor f_α , and the gap (“shifted in the $\ln \tau$ axis”) between both traces in an Arrhenius diagram underscores the distinction between all three dispersion zones $\{a, \alpha, \beta\}$, also.

This conclusion is supported by heat capacity spectroscopy (HCS), which indicates [9,12] unambiguously an onset of entropy fluctuation $\Delta S^2 \sim \Delta C_p \sim (T_{\text{on}} - T)$ in the splitting region in substances where the α onset is in the 10 kHz frequency region. HCS in poly(*n*-hexyl methacrylate) (PnHMA) [13], where the onset frequency is near the middle of the HCS frequency window, shows a clear distinction between a and α (β is not calorimetrically active) by a saddle in the C_p'' contour map, which is not seen in the ε'' contour

map because the dielectric β contribution is large in PnHMA. This is a new piece in the long list of qualitative changes in the crossover region [4].

The nearly parallel course of the α and β_{eff} traces in the Arrhenius diagram Fig. 1(a) implies, in the light of the product ansatz Eq. (2) for β_{eff} and the strong temperature dependence of f_α , a complicated balance between the relaxation times (τ_α, τ_β) and the shape parameters of the extrapolated φ_β and φ_α functions. Such a balance cannot be proved as yet, since the dielectric data are rather uncertain for $f > 10^6$ Hz; see Fig. 10 of [2].

The dielectric merging scenario [Figs. 1(a) and 1(b)] is hard to grasp with respect to tracing an α relaxation in the Arrhenius diagram for temperatures higher than the arrow temperature \downarrow (T_{on} in Fig. 2) where the f_α strength tends to zero.

It can also be seen from [2] that dielectric and neutron spin echo spectroscopy (NSE) reflect different facets of the dynamic glass transition. Two illustrative examples: (i) the mean β relaxation time from NSE is two decades faster than from dielectrics; (ii) the α relaxation in NSE shows a strongly Q -dispersive power law, whereas dielectrics shows, after an additive analysis, a normal $\varepsilon''(\log \omega)$ peak. A third example follows from the general consideration mentioned above. The dielectric relaxation is heavily influenced by mutual vector compensation of neighbor dipoles. In Ref. [9] it is shown that the dielectric intensity of α and ε_∞ increases when *n*-butylmethacrylate, *n*BMA, is copolymerized with the nonpolar styrene. This can only be explained by an increasing breakdown of \pm dipole compensation in PnBMA by the styrene monomers. Such a compensation is not directly reflected by a density correlation.

As a general strategy, it seems better to use the different responses to find facets of the complex phenomenon of glass transition, and to try afterwards to construct a consistent picture of the complex situation from the different facets, than to treat different responses with the same or similar arguments and evaluation methods.

V. CONCLUSION

The method used by Arbe *et al.* for the evaluation of dielectric data is not suited for the crossover region of dynamic glass transition.

ACKNOWLEDGMENTS

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