





Arriving at the most plausible interpretation of the dielectric spectra of glycerol with help from quasielastic γ -ray scattering time-domain interferometry

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Glycerol is one of the glass-forming liquids selected by Robert H. Cole in 1950 to start his study of molecular dynamics by dielectric spectroscopy. Seventy-one years have gone by and remarkably no consensus has been reached on the nature and identity of the relaxation processes observed in the dielectric spectra. The macroscopic dielectric relaxation data allow different interpretations to yield contrasting results, and it is not possible to determine which one is most plausible. Coming to the rescue is the application of the nuclear γ -resonance time-domain interferometry (TDI) to glycerol by Saito *et al.* [*Phys. Rev. E* **105**, L012605 (2022)]. Their microscopic TDI data potentially can decide which interpretation of the dielectric spectra of glycerol is most plausible. The attempt was made by Saito *et al.*, but there is a problem in their analysis of the dielectric data of glycerol and hence their conclusion is untenable. In this paper, we critically compare four major interpretations with the TDI data in an effort to identify the most plausible interpretation of the relaxation processes constituting the dielectric spectra of glycerol.

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I. INTRODUCTION

A recent paper published in this journal by Saito *et al.* [1] reported a microscopic study of the molecular dynamics of glycerol by quasielastic γ -ray scattering using time-domain interferometry (TDI) [2–4]. The TDI probes molecular dynamics over the time range from 10^{-9} to 10^{-5} s and scattering vectors q ranging from 9.6 to 58 nm^{-1} . Hence the technique is ideal for microscopic study of the cooperative α -relaxation together with the more local secondary relaxation over a wide range of lengthscales, $\xi = 2\pi/q$, and relaxation times. Before the TDI study of glycerol by Saito *et al.*, the technique had been applied to study the primary structural α -relaxation and the secondary relaxation of the van der Waals liquid, orthoterphenyl (OTP) [5], the amorphous polymer, 1,4-*cis-trans* polybutadiene (PB) [6], the monohydroxyl alcohol, 5-methyl-2-hexanol (5M2H) [7], and 1-propanol [8]. All four of these glass-formers had been studied before by dielectric spectroscopy to reveal in addition to the structural α -relaxation the presence of a well-resolved secondary β -relaxation having properties strongly connected to that of the α -relaxation [9–14], and such β -relaxation is exclusively called Johari-Goldstein (JG) β -relaxation to distinguish it from other trivial secondary relaxations. The TDI data of OTP, PB, 5M2H, and 1-propanol were reexamined in conjunction with dielectric relaxation data, and the microscopic TDI JG β -relaxation time $\tau_\beta(q, T)$, which is q -dependent, was compared with the macroscopic dielectric JG β -relaxation time $\tau_\beta(T)$ [15]. The observed increase of $\tau_\beta(q, T)$ on decreasing

q verified that the JG β -relaxation observed by dielectric spectroscopy is heterogeneous and is comprised of processes with different lengthscales. Processes with longer lengthscales have longer relaxation time [10,12–14]. The TDI $\tau_\beta(q, T)$ at some q significantly larger than q_{max} at the first peak of the static structure factor $S(q)$ was shown [15] to coincide with the primitive relaxation times $\tau_0(T)$ of the coupling model [10,12]. The coincidence verifies that the primitive relaxation of the coupling model is very local and is the precursor of the q -dependent distribution of relaxation times of the JG β -relaxation at lower q values. It also explains why the dielectric JG β -relaxation times $\tau_\beta(T)$ are approximately equal to $\tau_0(T)$ as found in many glass-formers including OTP, PB, 5M2H, and 1-propanol. The advance is a microscopic understanding of the distribution of processes composing the JG β -relaxation and its relation to the primitive relaxation and the α -relaxation.

Glycerol is different from OTP, PB, 5M2H, and 1-propanol because the supposedly universal JG β -relaxation was not resolved in its dielectric relaxation spectra. Observed instead is excess loss on the high-frequency side of the α loss peak over and above the fit by either the Cole-Davidson function [16,17] or the Fourier transform of the Kohlrausch-Williams-Watts (KWW) stretched-exponential correlation function [10,12,18,19],

$$\varphi(t) = \exp[-(t/\tau_\alpha)^{1-n}]. \quad (1)$$

The excess loss is referred to as the excess wing (EW), and it can be described by a power law $\nu^{-\lambda}$ with $\lambda \approx 0.5$ over a limited frequency range. Broadband dielectric spectra reveal that, at higher frequencies, the loss shows an even weaker frequency dependence before it starts to increase again

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towards a peak in the THz range, termed the boson peak in some publications [16,17]. This shallow loss minimum, which is a universal feature of glass-forming liquids, was predicted and explained by the mode-coupling theory of the glass transition [17]. However, it can also be well understood within the extended coupling model, predicting a weakly frequency-dependent loss region arising from caged molecular motion, referred to as the nearly constant loss (NCL) [10,12]. The NCL can be approximately described by a power law $\nu^{-\delta}$ with δ a small positive number. Within the coupling model, the NCL is also expected to show up at low temperatures in systems with excess wing or a JG β -relaxation. Indeed, for glycerol the power law with δ typically falling in the range from 0.1 to 0.2 at temperatures near and below $T_g = 185$ K (see Fig. S1 in the Supplemental Material [20]) can also be identified with the NCL.

The macroscopic dielectric data are indiscriminate enough to allow totally different assumptions and procedures to analyze the data and extract the supposedly omnipresent JG β -relaxation of glycerol, and to deduce its relaxation time $\tau_\beta(T)$ and its relation to the α -relaxation time τ_α . Unsurprisingly, very different results of $\tau_\beta(T)$ were reported by three interpretations all accepting that the JG β -relaxation is present in glycerol but is not resolved. The current TDI study of the microscopic dynamics of glycerol by Saito *et al.* [1] has the potential of finding out which interpretation is closer to the truth.

The first interpretation is based on the assumption that the contributions to dielectric relaxation from the JG β -relaxation and α -relaxation are independent and additive [16,18,21,22]. Representing the JG β by a Cole-Cole function,

$$\varepsilon_\beta^*(\nu) = \Delta\varepsilon_\beta/[1 + (i2\pi\nu\tau_{CC})^\mu], \quad (2)$$

and the α -relaxation by the Cole-Davidson function [16,21,22] or the Fourier transform of the KWW function [18], the sum of the two were used to fit the loss spectra (see, e.g., Figs. S2 and S3 of the Supplemental Material [20]). Determined by the fit is the value of $\tau_{CC}(T)$, which is identified as the JG β -relaxation time τ_β and shown in the inset of Fig. S3 of the Supplemental Material [20] for both choices of the α -peak fit function. For the KWW function, the deduced τ_β values are somewhat closer to τ_α than for Cole-Davidson. This arises partly from the somewhat different curve shapes of the two peak functions (see Ref. [20] for a detailed discussion), but it also mirrors the considerable uncertainty of τ_β due to the overlap of the β -relaxation with the α loss peak [16]. As shown in Ref. [18] and discussed below, the obtained $\tau_\beta(T)$ agrees reasonably with the predictions of the coupling model. As mentioned above, within the coupling model, at low temperatures the NCL is assumed to become part of the high-frequency flank of the Cole-Cole function used to represent the JG β -relaxation because the power μ in Eq. (2) coincides with δ (see Fig. S3 of the Supplemental Material [20]). In other words, within the coupling model the high-frequency flank of the very broad JG β -relaxation represented by the Cole-Cole function also represents the NCL.

The second interpretation from the paper by Gainaru *et al.* [22] has the presence of a β -relaxation, but it has smaller dielectric strength and much shorter relaxation times $\tau_\beta(T)$

compared with $\tau_{CC}(T)$ in the Cole-Cole function of the first interpretation. It considers the loss spectrum at temperatures close to or below T_g as contributed by the sum of three contributions: (i) the α -loss peak with its high-frequency flank having the $\nu^{-\beta}$ -dependence and $\beta \approx 0.6$, (ii) an EW contribution of $C\nu^{-\gamma}$ with $\gamma = 0.2$ and C an adjustable parameter, and (iii) an additional β -relaxation. For systems without a clearly discernible β -relaxation peak, as glycerol, within this framework a weak β -relaxation is revealed after phenomenologically subtracting $C\nu^{-\gamma}$ of the EW from the dielectric loss data. Note that the EW, $C\nu^{-\gamma}$ with $\gamma = 0.2$, in this second interpretation is different from the EW in the first interpretation, and is entirely different from EW with $\nu^{-\lambda}$ and $\lambda \approx 0.5$ in Refs. [10,12,18], although all are referred to as the EW. This second interpretation is limited in capability of yielding results of $\tau_\beta(T)$ only at temperature near or below T_g [23].

The third interpretation is based on the coupling model (CM) [10–15,18], which predicts that its primitive relaxation is the precursor and the earlier part of the distributed processes constituting the JG β -relaxation. Thus, the primitive relaxation time $\tau_0(T)$ is shorter than the dielectric JG β -relaxation time $\tau_\beta(T)$, but nevertheless both are approximately equal in order of magnitude, i.e.,

$$\tau_\beta(T) \approx \tau_0(T), \quad (3)$$

as verified in many glass-formers [9–15,18]. Since the primitive relaxation is universal, the CM asserts that the JG β -relaxation is omnipresent in any glass-former. In the case of glycerol, the JG β is hidden under the intense α -loss peak and unresolved, and it transpires as the EW. As can be seen in Fig. S1 of the Supplemental Material [20], the primitive relaxation frequency f_0 is located within the EW. As shown in Ref. [18], even when using the additive approach of the first interpretation, the obtained τ_β values agree reasonably well with the CM prediction, Eq. (3).

The microscopic TDI measurements of glycerol by Saito are timely to resolve the three different interpretations of its dielectric relaxation data resulting in different characterizations of the unresolved JG β -relaxation. Even more timely for the TDI data of glycerol is to critically judge the validity of a revolutionary interpretation of the dielectric spectra of polar molecular glass-formers including glycerol [24,25]. This novel interpretation proposes that the dielectric loss peak is composed of an intense Debye-like contribution from cross-correlation of dipoles in addition to a weak and slightly faster self-correlation contribution of dipoles. The latter has the broad generic shape with the $\nu^{-0.5}$ -dependence at high frequencies as seen in glycerol by photon correlation spectroscopy. The purpose of this paper is to bring the TDI data of glycerol to bear on the four different interpretations of the dielectric spectra, and in the process arrive at the most plausible interpretation of the dielectric relaxation spectra of glycerol.

II. RESULTS AND DISCUSSIONS

The main task of this paper is to make use of the microscopic TDI data of glycerol, $\tau_\alpha(q, T)$ and $\tau_\beta(q, T)$, from Saito *et al.* to critique the three different interpretations of

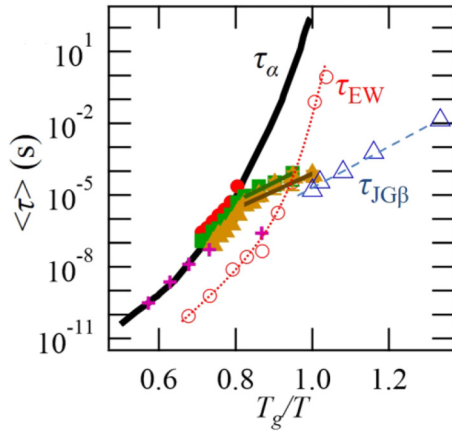


FIG. 1. This is a reproduction of Fig. 3(b) of Saito *et al.* [1], but the caption is rewritten to bring out the points discussed in the current paper. The closed symbols are TDI data $\tau_\alpha(q, T)$ and $\tau_\beta(q, T)$ at different q 's. The solid line is the α -relaxation time from dielectric measurements [16]. The open circles originally stand for the JG β -relaxation times $\tau_{CC}(T)$ in Ref. [16] obtained by the fit with the sum of a Cole-Davidson and a Cole-Cole function in the first interpretation. The label $\tau_{CC}(T)$ was changed by Saito *et al.* to τ_{EW} to represent “the timescales of EW τ_{EW} determined by assuming a single peak for EW in the dielectric relaxation spectra” [1]. As discussed in the text, the relabeling and reinterpretation by Saito *et al.* are invalid because EW is a power law and no relaxation time can be defined. Empty triangles are the JG β -relaxation times obtained from the second interpretation of Ref. [22]. Dotted and dashed lines are guides for the eye. Crosses are the collective relaxation times determined by NSE at $q = 0.74 \text{ nm}^{-1}$ [25].

dielectric data all advocating the presence of a JG β -relaxation albeit with different results of its relaxation times. Moreover, the TDI data provide a unique opportunity to test the radical interpretation of the dielectric spectra of polar molecular glass-formers including glycerol proposed recently [24,25], which rejects the presence of the JG β -relaxation. Before these tasks can be performed, we will summarize the conclusions of Saito *et al.* [1] reached in comparing their TDI data with dielectric and neutron spin echo (NSE) measurements, which are different from our own conclusions based on the third interpretation. For this purpose, we reproduce Fig. 3(b) of Saito *et al.* [1] as our Fig. 1 where the TDI α - and the JG β -relaxation times, $\tau_\alpha(q, T)$ and $\tau_\beta(q, T)$, were compared with the dielectric relaxation times from the first interpretation [16] and the second interpretation [23]. These are the dielectric $\tau_\alpha(T)$ and $\tau_{CC}(T)$ from the first interpretation above T_g , and the $\tau_\beta(T)$ near and below $T_g = 185 \text{ K}$ from the second interpretation. Included also is the relaxation time τ_{NSE} at $T_g/T = 0.87$ or $T = 213 \text{ K}$ determined in the NSE experiment by Gupta *et al.* [26] at $q = 0.74 \text{ nm}^{-1}$ much smaller than that of TDI and corresponding to a spatial scale of $2\pi/q \sim 8.5 \text{ nm}$.

It is important to point out that the dielectric data labeled $\tau_{CC}(T)$ in the paper by Lunkenheimer and Loidl [16] and in the first interpretation were clearly identified as the JG β -relaxation times (see the captions of Figs. 10 and 11 in Ref. [16]). However, Saito *et al.* observed that the temperature

dependence of the dielectric $\tau_{CC}(T)$ is non-Arrhenius like the α -relaxation time $\tau_\alpha(T)$ (see Fig. 1), and very different from that of the TDI $\tau_\beta(q, T)$. Since Saito *et al.* had definitively identified $\tau_\beta(q, T)$ with the JG β -relaxation times, naturally they were forced to associate $\tau_{CC}(T)$ with another process different from the JG β -relaxation. In fact, they associated $\tau_{CC}(T)$ with the excess high-frequency component of the α process given by $C\nu^{-\gamma}$ with $\gamma = 0.2$ in the second interpretation proposed by Gainaru *et al.* [23]. There it was also called the excess wing contribution, denoted by the acronym EW, and this is the reason why Saito *et al.* [1] relabeled $\tau_{CC}(T)$ as τ_{EW} in their Fig. 3(b) or Fig. 1 herein. Saito *et al.* also observed that the NSE relaxation time $\tau_{NSE}(T)$ at $T_g/T = 0.87$ is close to $\tau_{CC}(T)$, and they relabeled it as well using τ_{EW} . Therefore, they identified the excess high-frequency component of the α process modeled by the Cole-Cole function in the first interpretation together with the NSE data as the EW of the second interpretation. However, one should be aware that the EW of Gainaru *et al.* is a power law $C\nu^{-\gamma}$, for which no characteristic time τ_{EW} can be defined. Hence, one should not reinterpret the dielectric JG β -relaxation in the first interpretation [16] and the NSE relaxation at $T_g/T = 0.87$ [26] as the EW in the second interpretation, and should not relabel $\tau_{CC}(T)$ and $\tau_{NSE}(T)$ using τ_{EW} as was done in Fig. 3(b) in Ref. [1] or Fig. 1 herein.

Furthermore, Saito *et al.* observed that the relaxation times $\tau_\beta(T)$ of the weak β -relaxation from Gainaru *et al.* at temperature near or below T_g seem to be a continuation of their TDI data of $\tau_\beta(q, T)$ at $q = 58 \text{ nm}^{-1}$ at temperatures from 220 K ($T_g/T = 0.84$ in Fig. 1) down to $T_g = 185 \text{ K}$. This led them to assert that the two are the same, and the $\tau_\beta(T)$ of Gainaru *et al.* are indeed the JG β -relaxation times. However, the data of the TDI intermediate scattering functions (ISFs) in the temperature range from 220 to 185 K and at $q = 58$ and 41 nm^{-1} shown in Figs. 2(c) and 2(d) of Saito *et al.* [1] are scanty, have large scatters, and hardly decay. Thus the reliability of the values of $\tau_\beta(q, T)$ from their ISF is low, and it is questionable to identify their values of $\tau_\beta(q, T)$ at temperatures from 220 down to 185 K with the $\tau_\beta(T)$ from Gainaru *et al.* at T_g and below, and use it to support the second interpretation of the dielectric relaxation spectra of glycerol. There is yet another problem in the endorsement of the second interpretation of dielectric spectra of glycerol by Saito *et al.* Long-time aging of glycerol up to $10^{6.5} \text{ s}$ at 179 K or $T_g/T = 1.036$ by Schneider *et al.* [22] found the emergence of a shoulder in the EW of the first interpretation, and this is evidence of the JG β -relaxation. The fit by the sum of the Cole-Davidson and the Cole-Cole function gave $\tau_{CC}(T) \approx 0.8 \text{ s}$ at $T = 179 \text{ K}$ [22] [see also Fig. S3(a) of the Supplemental Material [20]], which is about 3.4 decades longer than τ_β of the weak β -relaxation in Gainaru *et al.* [23] at $T_g/T = 1.036$. This large discrepancy is evident by inspection of Fig. 2 to be introduced later, and it casts doubt on the validity of τ_β in the second interpretation. There is no doubt that the microscopic TDI data of the JG β -relaxation and its relaxation times $\tau_\beta(q, T)$ provided by Saito *et al.* [1,4] are fundamental and consequential. However, the conclusions by Saito *et al.* are only based on the comparisons of results from TDI exclusively with the dielectric relaxation data from the first and second interpretations. Therefore, the

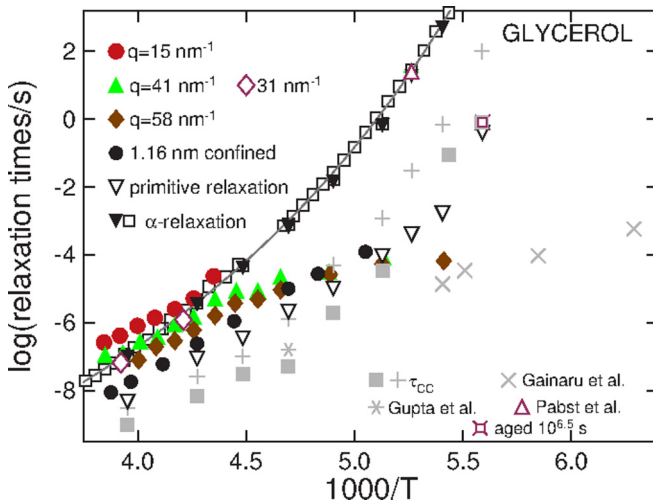


FIG. 2. The closed red, green, and brown symbols are TDI relaxation times $\tau_\alpha(q, T)$ and $\tau_\beta(q, T)$ at different q 's. The black open squares and closed gray signs are the mean α -relaxation times from dielectric measurements in Refs. [16,18], respectively. The solid line is a fit of these data by the Vogel-Fulcher-Tammann law [29]. The closed gray squares and plus signs are the JG β -relaxation times $\tau_{CC}(T)$ obtained by the fits with, respectively, the sum of a Cole-Davidson and a Cole-Cole function [16] and the sum of a Fourier transform of the KWW function and a Cole-Cole function [18] in the first interpretation. The open gray signs are the calculated primitive relaxation times $\tau_0(T)$. The black closed circles are $\tau_{\alpha,conf}(T)$ of glycerol confined in a microporous zeolitic imidazolate framework [30]. The * represent $\tau_{NSE}(T)$ at one temperature at $q = 0.74 \text{ nm}^{-1}$ [25]. The multiplication signs are the JG β -relaxation times obtained from the second interpretation of Ref. [22]. The magenta square decorated at four corners represents the equilibrium JG β -relaxation time at 179 K after aging for $10^{6.5} \text{ s}$ [21]. The lone magenta open triangle and labeled by Pabst *et al.* shows the prediction of the authors in Ref. [24] for glycerol when studied by TDI.

impact of the microscopic $\tau_\beta(q, T)$ TDI data on arriving at the most plausible interpretation of the macroscopic dielectric relaxation time is still unknown, and further consideration is needed.

Here we employ the third scenario based on the CM to interpret the TDI data. Its key prediction is the universal presence of the JG β -process in all glass-forming liquids whether resolved or not, and the JG β and the primitive relaxation times, $\tau_\beta(T)$ and $\tau_0(T)$, are approximately equal [see Eq. (3)], although $\tau_0(T)$ is expected to be shorter than $\tau_\beta(T)$. The time-honored CM equation,

$$\tau_\alpha(T) = [(t_c)^{-n(T)} \tau_0(T)]^{1/[1-n(T)]}, \quad (4)$$

enables $\tau_0(T)$ to be calculated from $\tau_\alpha(T)$. In the equation, t_c is 1–2 ps for molecular and polymeric glass-formers and was determined from quasielastic neutron scattering experiment [12,27–29] and atomistic molecular-dynamics simulations of *cis*-1,4 polybutadiene [30], and $(1-n)$ is the fractional exponent of the KWW stretched-exponential correlation function in Eq. (1). In Ref. [18], we calculated by Eq. (4) the values of $\tau_0(T)$ at a number of temperatures for which both $\tau_\alpha(T)$ and the stretch exponent $[1-n(T)]$ of the KWW function are

known from fits of the dielectric loss of the α -relaxation. The results of $\tau_0(T)$ are shown in Fig. 2, together with $\tau_\alpha(T)$ [16,18,31] and the TDI data $\tau(q, T)$ at four values of q [1].

The prediction $\tau_\beta(T) \approx \tau_0(T)$ has been tested successfully in many glass-formers where the JG β -relaxation is resolved and $\tau_\beta(T)$ determined unequivocally [9–15]. These cases include xylitol and sorbitol, which are higher members of the polyalcohols than glycerol. From Eq. (4) the invariance of the ratio τ_α/τ_β to changes of T and pressure P at any fixed τ_α value was derived [13], and remarkably this property is generally found by experiments, as well as the related prediction that τ_β and τ_α are functions of the same thermodynamic scaling variable TV^ν [14]. The JG- β relaxation is the precursor of the α -relaxation, and from the strong connection between the two processes in properties it is clear that contributions to dielectric loss from the two processes are not independent and not additive, different from the practice in the first interpretation. Thus, the values of $\tau_{CC}(T)$ deduced by the analysis in the first interpretation are not expected to accurately represent that of the JG- β relaxation. Moreover, as pointed out in Ref. [16], due to the superposition of most of the CC peak by the α -relaxation peak, essentially only a lower limit for τ_{CC} can be reliably deduced from the fits performed according to the first interpretation. This readily explains why the $\tau_{CC}(T)$ values shown in Fig. 2 are so different in magnitude and temperature dependence from those of the TDI $\tau_\beta(q, T)$ at $q = 41$ and 58 nm^{-1} . Please note that in Fig. 2, we show $\tau_{CC}(T)$ resulting from two alternative evaluations assuming a Cole-Davidson (closed squares) [16] or a KWW function (plusses) [18] for the α relaxation. As pointed out in Ref. [18], $\tau_{CC}(T) \approx \tau_\beta(T)$ from the latter approach quite nicely match $\tau_0(T)$, in accord with Eq. (3). However, due to the above-mentioned ambiguities of the evaluation within the first interpretation, the TDI data certainly represent a much better estimate of τ_β . The fact that $\tau_{CC}(T)$ has a non-Arrhenius temperature dependence, just as $\tau_\alpha(T)$, led Saito *et al.* to identify $\tau_{CC}(T)$ with $\tau_{EW}(T)$ of the excess high-frequency component of the α process (EW), but this is untenable because EW has no characteristic time.

As mentioned in the Introduction, in the cases of OTP, PB, 5M2H, and 1-propanol, the predicted $\tau_0(T)$ is in agreement with $\tau_\beta(T)$ of the resolved JG β -relaxation and also with $\tau_\beta(q, T)$ from TDI at some larger q values at temperatures above T_g . The compatibility of the prediction of the CM with the resolved JG β -relaxation implies similar success in glycerol by use of the third interpretation based on the CM. While its prediction, Eq. (3), is approximately fulfilled for $\tau_{CC}(T)$ deduced within the first scenario, a more stringent test is provided by comparing the results of $\tau_0(T)$ with the TDI $\tau(q, T)$ data, which for high q directly reflect the β -relaxation dynamics. As mentioned before when introducing the approximate Eq. (3), $\tau_0(T)$ is expected to be shorter than the JG β -relaxation time $\tau_\beta(T)$ because the primitive relaxation is the start of the distribution of processes composing the JG β -relaxation. This fact explains why $\tau_0(T)$ revealed in Fig. 2 are shorter than $\tau_\beta(q, T)$ for $q = 31, 41,$ and 58 nm^{-1} by about 1 decade at higher temperatures and smaller at lower temperatures.

There is another way to directly obtain $\tau_\beta(T)$ of glycerol by confining it in the microporous zeolitic imidazolate

framework (ZIF-8) with well-defined pore diameters of 1.16 nm and making dielectric measurements [32]. The fast process in the central part of the pores has relaxation times $\tau_{\alpha,\text{conf}}(T)$ much shorter than $\tau_{\alpha}(T)$ of bulk glycerol and having a temperature dependence weaker than the super-Arrhenius temperature of the latter. The cooperativity lengthscales $L_{\text{corr}}(T)$ of bulk glycerol were found to be larger than the pore size of ZIF-8 over the temperature range studied, and also the density of the glycerol in the pore is significantly lower than bulk. Consequently, cooperativity of the α -relaxation of glycerol confined in ZIF-8 is drastically reduced. Devoid of intermolecular coupling and cooperativity, $\tau_{\alpha,\text{conf}}(T)$ should be nearly the same as the primitive relaxation time $\tau_0(T)$ for glycerol. This is indeed found in glycerol [33], as shown in Fig. 2, and in another polar glass-former, prilocaine, also having unresolved JG β -relaxation [34,35]. The values of $\tau_{\alpha,\text{conf}}(T)$ are slightly longer than those of $\tau_0(T)$ calculated from $\tau_{\alpha}(T)$, and in better agreement with the TDI $\tau_{\beta}(q, T)$ for $q = 31, 41, \text{ and } 58 \text{ nm}^{-1}$. The exceptions occur at the two lower temperatures of about 185 K ($T_g/T = 1$) and 205.5 K ($T_g/T = 0.9$), where $\tau_{\beta}(q, T)$ for $q = 58 \text{ nm}^{-1}$ are much shorter than $\tau_{\alpha,\text{conf}}(T)$ and $\tau_0(T)$. Notwithstanding, these two exceptions can be ignored because of the large uncertainty of the values of $\tau_{\beta}(q, T)$ deduced from insufficient TDI data of limited quality at these two temperatures [see Fig. 2(d) in Saito *et al.*]. On the other hand, the good agreements of the microscopic $\tau_{\beta}(q, T)$ with $\tau_{\alpha,\text{conf}}(T)$ and $\tau_0(T)$ lead us to conclude that the most plausible or compatible interpretation of the macroscopic dielectric relaxation of glycerol is the third one based on the CM.

One can observe from Figs. 1 and 2 that the TDI $\tau_{\alpha}(q, T)$ at $q = 15 \text{ nm}^{-1}$ are longer than the dielectric $\tau_{\alpha}(T)$ especially at higher temperatures. The origin of the discrepancy is not clear, but a down shift of half a decade of $\tau_{\alpha}(q, T)$ brings them in better agreement with $\tau_{\alpha}(T)$. The same shift applied to the TDI $\tau_{\beta}(q, T)$ for $q = 31, 41, \text{ and } 58 \text{ nm}^{-1}$ also brings them in better agreement with $\tau_{\alpha,\text{conf}}(T)$ and $\tau_0(T)$. The results are shown in Fig. S4 of the Supplemental Material [20].

Shown by the black inverted triangle in Fig. 2 is the value of $\log_{10}[\tau_0(T)/\text{s}] = -0.4$ at $T = 179 \text{ K}$ (i.e., $1000/T = 5.59$) calculated by Eq. (4) with $\tau_{\alpha}(T)$ of the master loss spectrum at 179 K obtained by shifting and superpositioning the loss data actually measured at the lowest temperatures (see Fig. S1 of the Supplemental Material [20]). It compares well in Fig. 2 with $\log_{10}[\tau_{\text{CC}}(T)/\text{s}] \approx -0.1$ obtained within the first interpretation from glycerol data measured after aging at 179 K up to $10^{6.5} \text{ s}$ by Schneider *et al.* [22] [see Fig. S3(a) of the Supplemental Material [20]]. By contrast, $\tau_{\text{CC}}(T)$ is about 3.4 decades longer than τ_{β} of the weak β -relaxation in the second interpretation.

Finally, we bring the microscopic TDI data of $\tau_{\alpha}(q, T)$ and $\tau_{\beta}(q, T)$ to bear on the recent and radical interpretation of the dielectric spectra of polar molecular glass-formers with large dielectric strength $\Delta\epsilon$ including glycerol [24,25]. According to this interpretation, the narrow dielectric loss peak of polar molecular glass-formers including glycerol is the sum of an intense Debye-like contribution from the cross-correlation of dipoles and a weaker one from the self-correlation term having a generic broad line shape with the $\sim\nu^{-0.5}$ dependence

at high frequencies. If glycerol is probed by nondielectric spectroscopy such as light scattering and TDI in the present case, the cross-correlation term is absent. TDI is a gamma-ray scattering method that does not depend on the size of the dipole moment of the molecules. TDI, actually, is one of the few techniques able to probe directly microscopic density fluctuations in the 10 ns–10 μs time range. The beating pattern contrast function that is experimentally obtained by TDI is proportional to the density correlation function and allows extracting the center-of-mass dynamics at a microscopic scale (within a volume selected by q , the momentum exchanged in the scattering process). Good agreement of TDI data with that of quasielastic neutron scattering has been found for some prototypical glass-formers [8]. So, by no means can a pure rotational cross-correlation term dominate the dynamics revealed by TDI. Within the context of the Pabst *et al.* and Gabriel *et al.* interpretation [24,25], like that of PCS spectra, the TDI spectra cannot be interpreted as the sum of self-correlation and cross correlation of dipoles. Instead, a single relaxation with the generic line shape should be observed by TDI, and its relaxation time at $1000/190 \text{ K} = 5.26 \text{ K}^{-1}$ can be taken from the light-scattering spectra in Fig. 3 of Ref. [24]. It is represented by the lone magenta open triangle labeled by Pabst *et al.* at the bottom in our Fig. 2. In contrast, the TDI experiment found not only the α -relaxation but also the JG β -relaxation. Furthermore, at $T = 220 \text{ K}$ and $q = 15 \text{ nm}^{-1}$ with $\tau_{\alpha}(q, T) = 10^{-4.6} \text{ s}$, the Kohlrausch exponent $\beta_{\text{KWW}} \equiv (1-n)$ of the TDI α -relaxation has the value of 0.7 given by Saito *et al.* [1], which is nearly the same as 0.72, the value of β_{KWW} from dielectric relaxation given in the inset of Fig. 4 in Ref. [18]. The agreement in the values of $\beta_{\text{KWW}}(T) = a + bT$ with $a = 0.43 (\pm 0.08)$ and $b = 1.4 \times 10^{-3} (\pm 0.2 \times 10^{-3}) \text{ K}^{-1}$ from TDI given by Saito *et al.* [1] and dielectric relaxation [18] holds not only at 220 K but also at other temperatures. For example, at 240 K, the value of 0.76 for β_{KWW} from TDI [1] is practically the same as the value of 0.74 for β_{KWW} from the dielectric [18]. Such larger values of $\beta_{\text{KWW}}(T)$ of the α -relaxation from TDI contradict the much broader generic line shapes with $\beta_{\text{KWW}} \approx 0.5$ expected by Refs. [24,25] when glycerol is probed by TDI, like that seen by light scattering at the same temperatures shown in Fig. 3 of Ref. [24]. Thus, the findings of the TDI experiment by Saito *et al.* rule out the radical interpretation of the dielectric spectra of glycerol and polar liquids in general. Moreover, a recent comparison by Becher *et al.* [36] of the dielectric spectra of the polyalcohols, glycerol, threitol, xylitol, and sorbitol shows no relation between the dielectric relaxation strength $\Delta\epsilon$ and relaxation stretching or β_{KWW} , leading them to conclude a contradiction of the claim by Pabst *et al.* The study of the polar tributyl phosphate (TBP) of Moch *et al.* [37,38] by performing oscillatory shear and physical aging experiments also demonstrates that close to T_g the timescales of the molecular flow and of the structural recovery are governed by the same collective dynamics which controls the dielectric response of TBP but not PCS.

On the other hand, the fact that the α -relaxations of glycerol probed by TDI and dielectric relaxation have the same $\beta_{\text{KWW}}(T)$ throws additional support to the CM interpretation being compatible with the dielectric spectra of glycerol. The larger $\beta_{\text{KWW}}(T)$ values from the KWW fits of the dielectric

spectra are therefore appropriate characterizations of its narrow frequency dispersions of the α -relaxation, and it is proper to use them to obtain the JG β -relaxation times $\tau_\beta(T)$ of glycerol by Eqs. (3) and (4).

III. SUMMARY AND CONCLUSIONS

Glycerol was the choice of Robert H. Cole [39,40] for the study of glass-forming molecules by dielectric spectroscopy. Seventy-one years have gone by, and yet, remarkably, the interpretation of dielectric spectra of glycerol in terms of the dynamic processes is still unsettled. Different interpretations of the dynamic processes composing the macroscopic dielectric loss spectrum have been proposed, but there is no definitive way to determine which one is close to the truth. Even neutron scattering experiments did not help. The quasielastic γ -ray scattering using time-domain interferometry (TDI) was applied very recently by Saito *et al.* to glycerol. This microscopic technique has the luxury of probing glycerol at a different scattering vector q ranging from 9.6 to 58 nm⁻¹,

and correspondingly the dynamics at lengthscales from 0.65 down to 0.11 nm. Consequently, the structural α -relaxation with relaxation times $\tau_\alpha(q, T)$ was found at $q = 15$ nm⁻¹, and the JG β -relaxation with relaxation times $\tau_\beta(q, T)$ was found at $q = 31, 41,$ and 58 nm⁻¹. The TDI experiment thus proves that the dielectric spectra of glycerol are composed of the unresolved JG β -relaxation in addition to the α -relaxation. Saito *et al.* compared their TDI data of the JG β -relaxation with that from dielectric spectroscopy, but they considered only two out of the four extant interpretations, which include the one from the coupling model (CM). We show that the CM interpretation of dielectric relaxation of glycerol has the widths of the frequency dispersion or the $\beta_{\text{KWW}}(T)$ values of the α -relaxation in quantitative agreement with that from the TDI experiment. Moreover, the JG β -relaxation times $\tau_\beta(T)$ from the CM interpretation are in good agreement with the $\tau_\beta(q, T)$ from TDI experiment at high q . Therefore, the results from the microscopic TDI experiment make it possible to arrive at the most plausible or compatible interpretation of the relaxation processes composing the macroscopic dielectric spectra of glycerol.

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- [1] M. Saito, M. Kurokuzu, Y. Yoda, and M. Seto, *Phys. Rev. E* **105**, L012605 (2022).
- [2] A. Q. R. Baron, H. Franz, A. Meyer, R. Ruffer, A. I. Chumakov, E. Burkel, and W. Petry, *Phys. Rev. Lett.* **79**, 2823 (1997).
- [3] M. Saito, M. Seto, S. Kitao, Y. Kobayashi, M. Kurokuzu, and Y. Yoda, *Hyperfine Interact.* **206**, 87 (2012).
- [4] M. Saito, R. Masuda, Y. Yoda, and M. Seto, *Sci. Rep.* **7**, 12558 (2017).
- [5] M. Saito, S. Kitao, Y. Kobayashi, M. Kurokuzu, Y. Yoda, and M. Seto, *Phys. Rev. Lett.* **109**, 115705 (2012).
- [6] T. Kanaya, R. Inoue, M. Saito, M. Seto, and Y. Yoda, *J. Chem. Phys.* **140**, 144906 (2014).
- [7] F. Caporaletti, S. Capaccioli, S. Valenti, M. Mikolasek, A. I. Chumakov, and G. Monaco, *Sci. Rep.* **9**, 14319 (2019).
- [8] F. Caporaletti, S. Capaccioli, S. Valenti, M. Mikolasek, A. I. Chumakov, and G. Monaco, *Nat. Commun.* **12**, 1867 (2021).
- [9] K. L. Ngai, *J. Chem. Phys.* **109**, 6982 (1998).
- [10] K. L. Ngai, *J. Phys.: Condens. Matter* **15**, S1107 (2003).
- [11] K. L. Ngai and M. Paluch, *J. Chem. Phys.* **120**, 857 (2004).
- [12] K. L. Ngai, *Relaxation and Diffusion in Complex Systems* (Springer, New York, 2011).
- [13] S. Capaccioli, M. Paluch, D. Prevosto, K. L. Li-Min Wang, and K. L. Ngai, *J. Phys. Chem. Lett.* **3**, 735 (2012).
- [14] K. L. Ngai and M. Paluch, *J. Non-Cryst. Solids* **478**, 1 (2017).
- [15] K. L. Ngai, *Phys. Rev. E* **104**, 015103 (2021).
- [16] P. Lunkenheimer and A. Loidl, *Chem. Phys.* **284**, 205 (2002).
- [17] P. Lunkenheimer, U. Schneider, R. Brand, and A. Loidl, *Contemp. Phys.* **41**, 15 (2000).
- [18] K. L. Ngai, P. Lunkenheimer, C. Leon, U. Schneider, R. Brand, and A. Loidl, *J. Chem. Phys.* **115**, 1405 (2001).
- [19] P. Lunkenheimer, A. Pimenov, B. Schiener, R. Böhmer, and A. Loidl, *Europhys. Lett.* **33**, 611 (1996).
- [20] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevE.105.054609> for the dielectric loss data at various temperatures, fits of the α -relaxation by the Fourier transform of the KWW function and the Cole-Davidson function, and the JG β -relaxation by the Cole-Cole function, and change of spectra after aging. Included are the TDI relaxation times $\tau_\alpha(q, T)$ and $\tau_\beta(q, T)$ shifted downward by 0.5 decade.
- [21] P. Lunkenheimer, *Dielectric Spectroscopy of Glassy Dynamics* (Shaker, Aachen, 1999).
- [22] U. Schneider, R. Brand, P. Lunkenheimer, and A. Loidl, *Phys. Rev. Lett.* **84**, 5560 (2000).
- [23] C. Gainaru, R. Kahlau, E. A. Rössler, and R. Böhmer, *J. Chem. Phys.* **131**, 184510 (2009).
- [24] J. P. Gabriel, T. Böhmer, P. Zourchang, F. Pabst, A. Helbling, P. Weigl, and T. Blochowicz, *Phys. Chem. Chem. Phys.* **22**, 11644 (2020).
- [25] F. Pabst, J. P. Gabriel, T. Böhmer, P. Weigl, A. Helbling, T. Richter, P. Zourchang, T. Walther, and T. Blochowicz, *J. Phys. Chem. Lett.* **12**, 3685 (2021).
- [26] S. Gupta, N. Arend, P. Lunkenheimer, A. Loidl, L. Stingaciu, N. Jalarvo, E. Mamontov, and M. Ohl, *Eur. Phys. J. E* **38**, 1 (2015).
- [27] J. Colmenero, A. Alegria, A. Arbe, and B. Frick, *Phys. Rev. Lett.* **69**, 478 (1992).
- [28] V. G. Sakai, J. K. Maranas, Z. Chowdhuri, I. Peral, and J. R. D. Copley, *J. Polym. Sci., Part B* **43**, 2914 (2005).
- [29] V. G. Sakai, J. K. Maranas, I. Peral, and J. R. D. Copley, *Macromolecules* **41**, 3701 (2008).
- [30] G. Tsolou, V. A. Harmandaris, and V. G. Mavrantzas, *J. Chem. Phys.* **124**, 084906 (2006).
- [31] P. Lunkenheimer, S. Kastner, M. Köhler, and A. Loidl, *Phys. Rev. E* **81**, 051504 (2010).
- [32] M. Uhl, J. K. H. Fischer, P. Sippel, H. Bunzen, P. Lunkenheimer, D. Volkmer, and A. Loidl, *J. Chem. Phys.* **150**, 024504 (2019).
- [33] K. L. Ngai, P. Lunkenheimer, and A. Loidl, *Phys. Chem. Chem. Phys.* **22**, 507 (2020).
- [34] G. N. Ruiz, I. Combarro-Palacios, S. E. McLain, G. A. Schwartz, L. C. Pardo, S. Cervený, and R. Macovez, *Phys. Chem. Chem. Phys.* **21**, 15576 (2019).
- [35] K. L. Ngai, Z. Wojnarowska, and M. Paluch, *Phys. Chem. Chem. Phys.* **22**, 9257 (2020).

- [36] M. Becher, Th. Körber, A. Döß, G. Hinze, C. Gainaru, R. Böhmer, M. Vogel, and E. A. Rössler, *J. Phys. Chem. B* **125**, 13519 (2021).
- [37] K. Moch, P. Münzner, R. Böhmer, and C. Gainaru, [arXiv:2103.04624](https://arxiv.org/abs/2103.04624).
- [38] K. Moch, P. Münzner, R. Böhmer, and C. Gainaru, *Phys. Rev. Lett.* (to be published).
- [39] D. W. Davidson and R. H. Cole, *J. Chem. Phys.* **18**, 1417 (1950).
- [40] D. W. Davidson and R. H. Cole, *J. Chem. Phys.* **19**, 1484 (1951).