Computational Evidence for the Crucial Role of Dipole Cross-Correlations in Polar Glass-Forming Liquids

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In this Letter, we analyze the dipole-dipole correlations obtained from the molecular dynamics simulations for strongly and weakly polar model liquids. As a result, we find that the cross-correlations' contribution to the system's total dipole moment correlation function, which is directly measured in the dielectric spectroscopy experiment, is negligible for weakly polar liquids. In contrast, the cross-correlations' term dominates over the self-correlations' term for the examined strongly polar liquid. Consequently, our studies strongly support the interpretation of the dielectric spectra nature of glass-forming liquids recently proposed by Pabst *et al*.

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Despite the fact that broadband dielectric spectroscopy (BDS) is an experimental technique commonly used to study molecular dynamics for more than 100 years [1,2], the comprehensive understanding of the nature of the obtained spectra is still missing [3,4]. Therefore, it is not surprising that the interpretation of the BDS spectral shape describing the structural relaxation is the subject of the endless and hot debate on the physics of glass-forming liquids [5–7]. In this context, the notable advantages of BDS—the extremely broad range of measured relaxation times (18 decades) [8] and diversity of studied materials [9]—make the disclosure of the fundamental features of BDS relaxation spectra even more puzzling. Hence, the supplementation of BDS spectra with results delivered by other experimental techniques probing the corresponding molecular motions is crucial [9]. One noteworthy technique is depolarized dynamic light scattering (DDLS), which, similar to BDS, is sensitive to molecular reorientations [10]. However, the simple comparison of BDS and DDLS spectra reveals significant differences. The stretching parameter describing the dielectric-loss peak corresponding to the α relaxation process usually varies from 0.5 to 0.9 for weakly and strongly polar liquids, respectively [4]. In contrast, DDLS spectra reveal a quasiuniversal shape of the stretching parameter value approximately equal to 0.5 [11].

Recently, a promising solution to the problem, and hence, entirely new light on the origin of the broadening of relaxation spectra registered by BDS, has been found by Pabst and co-workers [12,13]. The authors postulated that the spectrum detected by a BDS originates from two types of correlations occurring between the molecules of polar liquids. The first one, which vanishes faster, describes how long a given molecule "remembers" its initial orientations. It is called self-correlation. The second one describes the time evolution of the other molecules with respect to the initial orientation of the chosen one, and it is called cross-correlation. In contrast to a BDS experiment, a DDLS probes mainly the self-correlations. Experimentally, it has been shown that the spectra obtained by both methods correspond to each other only for the weakly polar liquids. This accordance was explained assuming a negligible role of the cross-correlations. However, when the polarity of molecules increases, the role of the cross-correlations presumably increases as well. Therefore, different values of the stretching parameter for the BDS and DDLS spectra are observed. Hence, one can expect that the narrower shape of the dielectric spectra results from the existence of noticeable cross-correlations. By extracting the DDLS spectrum from the BDS spectrum, Pabst *et al.* tried to reveal the nature of the cross-correlations' spectral shape. Performing such an analysis, they pointed out that the shape of the cross-correlations' spectrum can be described by the Debye function (for an illustration, see Fig. 1).

At this point, it must be noted that the common interpretation of the spectra broadening relates this phenomenon to the existence of the relaxation time distribution [14–16]. Consequently, Pabst *et al.*, suggesting that the separation of timescales of the self- and cross-correlations is the main factor leading to the broader shape of the dielectric spectrum, shed new light on the problem of the proper interpretation of the BDS results. Moreover, their postulate is supported by the theory proposed by Déjardin *et al.* [17,18], according to which the response of a pair of dipoles consists of the two relaxation processes associated with the single and collective molecular motions. The relaxation times of those processes depend on the parameter $\lambda \sim \mu^2$ (μ is a molecular dipole moment), an increase of which separates the timescales of both processes. Hence, the experimentally observed correlation between the dielectric strength and the shape of the dielectric-loss peak can be

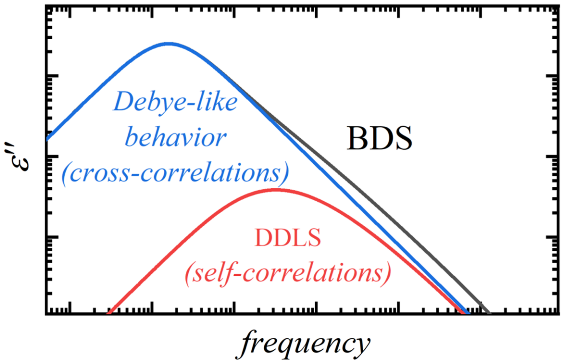

FIG. 1. The schematic representation of BDS and DDLS spectra is presented. The black line consists of two relaxation processes resulting from self- (red line) and cross- (blue line) correlations. Cross-correlations are characterized by Debye-like behavior, whereas self-correlations are described by the decay function with stretching parameter equal to 0.5.

qualitatively rationalized [13]. Furthermore, the recent experimental studies devoted to strongly polar liquid revealed that two characteristic timescales are visible during the aging process [19]. The one process mimics the generic structural relaxation toward the equilibrium, whereas the second one is ascribed to the evolution of the cross-correlations' mode. Interestingly, a similar experiment performed for weakly polar liquid with negligible dipole-dipole interactions results in a recovery process exhibiting a single exponential character. However, it must be stressed that, so far, there is no direct experimental evidence that the cross-correlations are marginal for weakly polar liquids. Moreover, it has not been directly shown that the cross-correlations decay slower and that their magnitude increases with the polarity of a molecule. Therefore, the proposed concept of the BDS spectra nature needs to be directly verified.

In this Letter, using the molecular dynamics simulations, we lay the cornerstone for any further studies based on proposed explanation of the origin of the BDS spectrum shape. For the two model systems, which differ exclusively in the value of the dipole moment, we calculate the self- and cross-correlations. Subsequently, we directly analyze their shapes and estimate their relative contributions to the correlation function of the system's total dipole moment, which is probed in the BDS experiment. Our findings confirm not only that the cross-correlations dominate for polar liquids but also that they relax in a manner similar to Debye-like behavior. Consequently, we verify the suggested interpretation of the BDS spectral shape for the first time and deliver strong evidence for its correctness.

The dielectric experiment is designed to monitor changes in the material polarization $\boldsymbol{P}$ induced by an external electric field E, which changes with time [16]. However, typically it is realized in the frequency domain, which means that the periodic $E(\omega)$ is used, where ω is the angular frequency. Then, the real ϵ' and the imaginary ϵ'' parts of the complex dielectric permittivity $\epsilon^*(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ reveal the existence of relaxation processes, i.e., around ω corresponding to the characteristic time of the given relaxation process τ, $\epsilon'(\omega)$ exhibits a steplike decrease, whereas the relaxation peak is detectable in $\epsilon''(\omega)$. This is due to both parts of $\epsilon^*(\omega)$ being related to the Fourier-Laplace transformation of the decay function of polarization $C(t) = \langle \boldsymbol{P}(t)\boldsymbol{P}(0)\rangle$, where $\langle\rangle$ denotes an ensemble average. In the simplest case of Debye-like behavior, $C(t)$ takes the exponential form $C(t) = A\exp[-(t/\tau)]$, where A is a parameter [20]. However, when the spectrum exhibits a broader shape, the Kohlrausch-Williams-Watts (KWW) function is commonly applied,

$$C(t) = A\exp\left[-\left(\frac{t}{\tau}\right)^{\beta_{KWW}}\right], \tag{1}$$

where β_{KWW} is the already mentioned stretching parameter. Since $\boldsymbol{P}(t)$ is proportional the total dipole moment of the system $\boldsymbol{M}(t) = \sum_{i=1}^{N}\boldsymbol{\mu}_i(t)$, $C(t)$ can be defined as

$$C(t) = \langle \boldsymbol{M}(0)\boldsymbol{M}(t)\rangle = \sum_{i=1}^{N}\sum_{j=1}^{N}\langle \boldsymbol{\mu_i}(0)\boldsymbol{\mu_j}(t)\rangle. \tag{2}$$

Finally, one can rewrite $C(t)$ as the sum of the self-correlation term

$$C_s(t) = \sum_{i=1}^{N}\langle \boldsymbol{\mu}_i(0)\boldsymbol{\mu}_i(t)\rangle, \tag{3}$$

and cross-correlation term

$$C_C(t) = \sum_{i=1}^{N}\sum_{j\neq i=1}^{N}\langle \boldsymbol{\mu}_i(0)\boldsymbol{\mu}_j(t)\rangle. \tag{4}$$

According to Eqs. (3) and (4), the information on the time evolution of the molecules' dipole moments is needed to calculate $C_s(t)$ and $C_c(t)$. Unfortunately, neither standard experimental method measures $\boldsymbol{\mu}(t)$. However, it is easily accessible in the computer simulations of molecular dynamics, which have another crucial advantage. Projecting model systems intended to a specific computational experiment, one has entire control of the physical differences between the created molecules. It is especially important because, the model systems, which are designed for an experiment to verify of the Pabst *et al.* interpretation of the BDS spectral shape, should possess identical molecular structures but differ in the value of μ. Then, the model representative of weakly polar liquids would exhibit the negligible cross-correlations' contribution to the total dipole correlation function; i.e., $C(t)$ should be dominated by $C_s(t)$. Contrarily, for the second model system possessing a substantially higher μ value, one might expect the evident role of $C_c(t)$ in $C(t)$. An attractive candidate for planned studies is the rhombuslike molecule (RM) [21–24], which consists of four atoms. Then, μ might be placed along one of two diagonals. It is worth mentioning that the shape of RM reflects the structural anisotropy of many van der Walls liquids and that the RM systems are relatively easy to supercool [23]. Following our previous studies, the used atoms represent carbon atoms, which create the benzene ring. Consistently, the bond length between the RM's atoms is around 0.15 nm (the tiny difference between the real length of the bond in the benzene ring and 0.15 nm results from the fact that one diagonal of RM is 2 times shorter than the other one). The stiffness of bonds, angles, and dihedrals, as well as the nonbonded interactions between the atoms of different molecules, are defined using the parameters of an optimized potentials for liquid simulations all-atom force field provided for the carbon atom of the benzene ring as well [25]. However, in order to create specific μ, we redefine the atoms' charges. In this way, the herein studied RMs are characterizes by μ equal to $0.386D$ and $3.86D$, which are arranged alongside the longer diagonal of the RM (this orientation impedes the crystallization of the RM systems [23]). As a starting point, we equilibrate the systems containing $N = 16\,384$ molecules at NVT conditions $V = 1643\ \mathrm{nm}^3$ and $T = 200$ K, at which $C(t)$ decays within accessible time of computer simulations. The Nose-Hoover thermostat [26–28], which is implemented in GROMACS software [29–33], provided constant temperature conditions. Simulation runs were performed using the velocity-Verlet integration scheme [34] with a time step equal to 0.001 ps. The applied cutoff for intermolecular interactions was set to 4.260 nm, which is 12 times longer than the σ parameter of the intermolecular interaction potential. Long-range dipole-dipole interactions have been realized by the use of the reaction field method [35,36]. The dielectric constant of the reaction field ϵ was predicted according to (classical from the BDS point of view) Onsager theory [37], which for the study herein, the nonpolarizable polar molecules take the form $[(\epsilon-1)(2\epsilon+1)/\epsilon] = (N_0\mu^2/\epsilon_0 k_B T)$ [38], where N_0 is the number of dipoles within the volume unit, ϵ_0 is the dielectric permittivity of vacuum, and k_B is Boltzmann's constant. In Supplemental Material [39] we show that the use of particle mesh Ewald summation gives identical results [40] and that the obtained results do not depend on the system size.

As we already mentioned, the BDS experiment uses the external electric field, which is applied to the sample. Therefore, we examine RM systems not only at equilibrium conditions but also when an outer disturbance is employed. Consequently, our computational experiment consists of three parts, which were repeated 50 times for each RM system. In the first step, we polarize the previously equilibrated system by applying a constant external electric field in direction z, E_z. It has to be noted that the applied E_z are equal to half of $0.1k_BT/\mu$, which ensures that our experiment is performed in the linear response regime [16]. In the next step, an applied external electric field is suddenly turn off, which enables the estimation of the relaxation functions of P directly probed in the BDS experiment. The final step is a standard simulation without an external field for 0.2 ns, which is carried out to calculate $C(t)$. The obtained results are presented in Fig. 2.

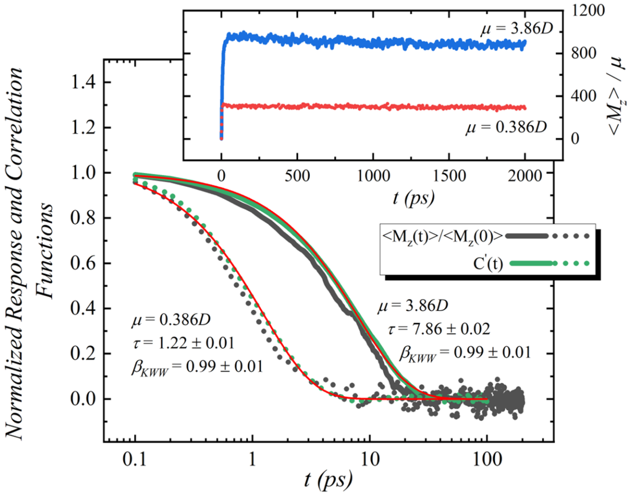

FIG. 2. The normalized response $\langle M_z(t)/M_z(0)\rangle$ and correlation $C'(t)$ functions are presented. The black lines (solid and dotted) represent the response functions and are calculated based on the results presented in the inset. The green lines (solid and dotted) are obtained from fluctuations at equilibrium conditions. The dotted lines depict results obtained for weakly polar liquid, whereas the solid ones are for strongly polar liquid. The red lines represent fits of $C'(t)$ by a decay function described by Eq. (1). Inset shows the time evolution of the system's total dipole moment in the z direction, which is forced by the applied external electric field. The blue line is obtained for strongly polar liquid, whereas the red line is for the weakly polar one. Note that, if all molecules are arranged parallel to E_z, $\langle M_Z\rangle/\mu = N$.

In the inset of Fig. 2, one might observe an average value of the dipole moment oriented in the z direction $\langle M_Z\rangle$, which in order to fairly compare the changes taking place within the systems, has been scaled by μ. Interestingly, already this part of our study reveals evident differences between both RM systems. The RM with a higher μ value (blue line) exhibits higher orientational polarizability, despite the corresponding E_z having been applied to both systems. It suggests the existence of additional contributions to $\boldsymbol{P}$, which might originate from a collective behavior of molecules. Another crucial observation is that both systems reach equilibrium within 2 ns. Hence, the applied E_z does not polarize the system anymore, and the system's reaction to an outer disturbance can be quantified during the second part of our experiment. When the external electric field is immediately removed, the system responds, which is observed by a decrease in $\boldsymbol{P}(t)$. As we already noted, $\boldsymbol{P}(t)$ can be quantified using $\boldsymbol{M}(t)$. However, in our case, only the component in the z direction is of interest. Therefore, in Fig. 2 we present the normalized function of the system's total dipole moment $\langle M_z(t)\rangle/\langle M_z(0)\rangle$, and the starting point is the time at which we turn off E_z. Also in this figure, one can observe evident differences between $\langle M_z(t)/M_z(0)\rangle$ for both systems. The RM system with a higher μ value relaxes slower (solid line) than the one with a smaller μ value (dotted line). Since our experiment is performed in the linear response regime, τ does not depend on the E_z magnitude. Moreover, in Fig. 2 we depict normalized $C(t)$, $C'(t) = C(t)/\langle \boldsymbol{M}(0)\boldsymbol{M}(0)\rangle$ calculated based on the third step of our experiment. It is crucial because according to the fluctuation dissipation theorem, the response of the system to external disturbance is related to the fluctuations at equilibrium [7] $C(t)$. As one can see, for both studied systems, $\langle M_z(t)/M_z(0)\rangle$ indeed corresponds to the fluctuations of a corresponding quantity at equilibrium. The slight differences result from a limitation in $\langle M_z(t)/M_z(0)\rangle$ averaging, which is done for 50 independent simulations, whereas $C'(t)$ is an average of 50 simulations and 1000 functions established from one simulation run. The correspondence of $\langle M_z(t)/M_z(0)\rangle$ and $C'(t)$ is crucial for further studies because we can employ simulations at equilibrium, which significantly improve the data statistics. At this point, it is also worth mentioning that a similar value of β_{KWW} for both systems can be justified by the fact that we examine thermodynamic conditions, which are far from the glass transition. The dependence of $C'(t)$ on the thermodynamic conditions is discussed later.

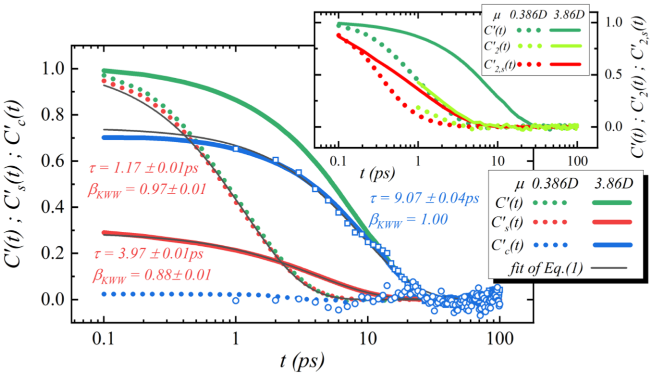

FIG. 3. The normalized total dipole correlation functions and their self- and cross-components are presented for two model systems. The dotted lines are calculated for a representative of weakly polar liquids, whereas solid lines are obtained for a strongly polar liquid. The cross-correlation's contributions are calculated according to the relationship $C'_c(t) = C'(t) - C'_s(t)$. The black line represents the fit of a decay function described by Eq. (1). The values of the stretching parameter are presented for self- and cross-correlation's contributions to the total dipole correlation function. The open symbols depict cross-correlation contributions calculated directly, i.e., according to Eq. (4). Because of the computational effort, the data are averaged over 50 independent functions (in contrast, the data presented as lines are averaged over 5000 independent functions). Inset presents the normalized total dipole correlation function as well as the total and self-correlation functions of the second Legendre polynomial for the two studied systems.

In Fig. 3, we present calculated $C'(t)$ and its contributions from self- and cross-correlations $C'_s(t) = C_s(t)/\langle \boldsymbol{M}(0)\boldsymbol{M}(0)\rangle$ and $C'_c(t) = C_c(t)/\langle \boldsymbol{M}(0)\boldsymbol{M}(0)\rangle$, respectively. Interestingly, even though $C'(t)$ exhibit similar shapes for both RM systems, the contributions to $C'(t)$ from the self- and cross-correlations are totally different. In the case of the weakly polar system (dotted lines), $C(t)$ is entirely dominated by the self-correlations. The role of $C_c(t)$ is marginal because it gives input to $C(t)$ at a level of less than 5%. However, a totally different situation takes place for the strongly polar liquid (see results for the second RM system). An increase in the μ value means that, due to stronger dipole-dipole interactions, the correlations between neighboring molecules become noticeable. This causes the role of $C_c(t)$ in the total dipole correlation function to increase. Consequently, we observe that $C_c(t)$ dominates over $C_s(t)$ for a RM system with high μ value (solid lines). However, in this case the role of $C_s(t)$ cannot be neglected because it is still at the level of 30%. Hence, our findings prove that BDS spectra reflect mainly self-correlations only for the weakly polar liquids. Therefore, for those systems exclusively, the BDS and DDLS experiments could correspond to each other. We would like to emphasize to the readers that, similar to previous suggestions, $C_s(t)$ vanishes faster than $C_c(t)$. It differs from the results obtained by Zhou and Bagchi [41] for the self-consistent continuum model of Nee and Zwanzig [42], who find that within the studied system a single particle orientational relaxation is slower from the collective orientational relaxation. The noted discrepancies might be caused by the absence of the translational motion in the examined dipolar lattice model. Nevertheless, our results are in accord with predictions of Déjardin *et al.* [17,18], who suggest that the collective mode relaxes slower than the single molecular one.

As we already noted, the role of self-correlations in the relaxation process cannot be negligible for a strongly polar system. Therefore, the corresponding BDS spectrum contains self- and cross-contributions, wherein the self-correlations give a smaller input located at higher frequencies. The latter might lead to spectra broadening (see schematic representation in Fig. 1), especially since our results reveal as well that $C_c(t)$ exhibits a narrower shape of the relaxation spectrum than $C_s(t)$ does. It directly reflects the postulate by Pabst *et al.* concerning the interpretation of the BDS spectrum. However, in the case of the DDLS spectrum the situation is suggested to be totally different. Namely, Pabst *et al.* claim that the DDLS spectrum originates from only the self-correlations because this experimental technique is insensitive to the cross-correlations. In the inset of Fig. 3, we present the calculated $C_2(t) = \sum_{i=1}^{N}\sum_{j=1}^{N}\langle P_2(u_i(0)u_j(t))\rangle$, which describes the dynamics of the anisotropic polarizability tensor probed by DDLS [P_2 is the second Legendre polynomial and $u_i(t)$ is a unit vector along the dipole moment of the molecule i at

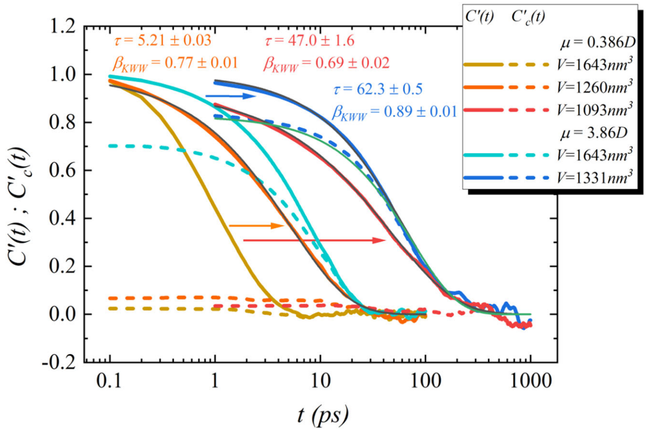

FIG. 4. The normalized total dipole correlation functions and their cross-components are presented for the two studied model systems at different thermodynamic conditions. The arrows indicate the compression of weakly (orange and red) and strongly (blue) polar liquids. The black lines depict the fit of the function described by Eq. (1) to the obtained data. The green line is a fit of the Debye function to the cross-correlations for the compressed strongly polar system.

time t] [43–45]. As can be observed, the self-component to $C'_2(t)$, i.e., $C'_{s,2}(t)$, overlaps $C'_2(t)$ in very good agreement independent of the molecular polarity. This observation is in accord with the results of the already performed computer simulations and experiments, which pointed out that the cross terms make only a small contribution to $C'_2(t)$ for molecular fluids [44,45]. Moreover, from the inset of Fig. 3 one can clearly notice the evident discrepancies between the decay processes of $C'(t)$ and $C'_2(t)$, i.e., $C'_2(t)$ decays faster and is broader, which is especially visible for a strongly polar system. At this point, we would like to mention that $C'_2(t)$ starts at a longer time than the other functions, which is because $C'_2(t)$ considers all pairs of molecules i and j, and therefore, its calculation [similar to $C_c(t)$] requires an enormous computational effort.

Finally, in Fig. 4 we present the evolution of $C'(t)$ and $C'_c(t)$ when the studied the systems approaching the glass transition, which have been realized by the isothermal compression. Comparing $C'(t)$ characterized by the similar relaxation times, one can see that $C'(t)$ for a weakly polar system is much broader. Furthermore, for this system, a slowing-down in molecular dynamics results in an evident change in β_{KWW} (from 0.99 to 0.77 and then to 0.69). Hence, one might suspect that β_{KWW} tends to the suggested value of 0.5. However, an examination of the corresponding thermodynamic conditions is a very challenging task due to the limitations of the computational experiment. Contrarily, for strongly polar liquid, $C'(t)$ changes only slightly; i.e., β_{KWW} of the corresponding functions changes from 0.99 to 0.89. Hence, the obtained $C'(t)$ follows not only the postulate by Pabst *et al.* but also the experimentally established correlation between the dipole moment value and the shape of the BDS spectrum [4]. The latter could be explained by the role of the cross-correlations in the system's relaxation process. For a weakly polar system, $C'_c(t)$ is marginal and persists on the same level for the majority of time. It means that the behavior of $C'(t)$ is determined solely by the self-correlations, which are much broader. On the other hand, $C'_c(t)$ visibly dominates $C'(t)$ for a strongly polar system. The decrease in the self-correlation is visible only at the initial stage of the relaxation process, which means that its contribution is observed at frequencies higher than the dielectric-loss peak. The latter results only in a tiny broadening of the spectrum because $C'_c(t)$ can be still described by the Debye-like behavior with very good accuracy.

Summarizing, in this Letter, we contribute to the recently proposed explanation of the differences of the results obtained by various experimental methods, i.e., BDS and DDLS. Our experiment delivers clear evidence for the existence of the direct relationship between the broadening of the dielectric spectra and the role of cross-correlations of the molecules' dipole moments. We present that the cross-correlations practically do not occur for weakly polar molecules and that for this system the corresponding spectrum is distinctly widened. Contrarily, the total dipole correlations function is almost entirely dominated by the cross term for strongly polar liquids. Since the cross-correlations are characterized by the less broad relaxation function, the corresponding dielectric spectrum is only slightly widened. In this case, self-correlations give a tiny contribution at the initial stage of the dielectric relaxation process. It implies that, as established in the literature, the relationship between the dipole moment value and the BDS spectral shape can be immediately justified. Therefore, our findings not only strongly support the postulate by Pabst *et al.,* but they also prove the existence of the experimentally observed correlation. Consequently, our Letter provides a cornerstone for the proper interpretation of the nature of a BDS spectrum.

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