Predicting the Density-Scaling Exponent of a Glass-Forming Liquid from Complex Dielectric Permittivity Measurements

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One of the challenging problems related to the liquid-glass transition phenomenon is establishing a link between the character of intermolecular interactions and the behavior of molecular dynamics. Introducing the density scaling concept, according to which dynamic quantities, e.g., viscosity or structural relaxation time (τ_α) measured at different thermodynamic conditions are expressed as a single universal curve if plotted against ρ^γ/T, led to significant progress in solving this problem since the scaling exponent γ defines the steepness of the repulsive part of the intermolecular potential. Herein, we found that relaxation dynamics of van der Waals and H-bonding glass formers, for which the Kirkwood factor (g_K) is an isomorph-invariant quantity, satisfy an alternative scaling, $\log\tau_\alpha$ vs $T(\Delta\varepsilon_s T)^{-\gamma}$. As a result, the exponent γ is determined from the temperature and pressure evolutions of τ_α and dielectric relaxation strength $\Delta\varepsilon$—both obtained in a single dielectric experiment, which makes the γ coefficient to be accessed in the future for an extensive database of glass-forming liquids.

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Understanding the molecular dynamics behavior of glass-forming liquids is essential to advance knowledge about glass formation and to design new materials with tailored properties. The molecular mobility of a given liquid can change substantially under relatively minor modifications of thermodynamic conditions [1]. Above the melting point (T_m), the molecules move rather independently with the relaxation time in the order of nano- to picoseconds. However, as the temperature decreases below T_m or pressure increases at a constant temperature, the viscosity of supercooled liquid continuously rises, and molecular dynamics slow down. It is commonly observed that the rate of molecular rearrangements changes during cooling significantly faster than predicted by the Arrhenius law [2–5]. This specific pattern of behavior is conventionally called the super-Arrhenius behavior.

It has long been debated to what extent the thermal and density fluctuations govern the super-Arrhenius behavior and what molecular factors determine the relative contributions of both these effects [6–11]. The insight into these challenging problems was made possible by developing high-pressure broadband dielectric spectroscopy (HPBDS) [12]. Specifically, isobaric and isothermal HPBDS measurements combined with $V_{\mathrm{sp}}(T,P)$ (PVT) data of various glass-forming liquids have shown that the ratio between activation energy at constant volume ($E_V = R(\partial\log\tau_\alpha/\partial T^{-1})|_V$) and activation energy at constant pressure ($E_P = R(\partial\log\tau_\alpha/\partial T^{-1})|_P$), E_V/E_P, which defines the relative contributions of thermal and molecular packing effects, is linked to the character of intermolecular interactions [13,14]. More precisely, it was pointed out that density and thermal fluctuations play the same role in the case of van der Waals liquids. In contrast, a much weaker effect of density is observed for ionic liquids and H-bonded materials due to long-range Coulombic or H-bonding interactions, respectively. These experimental insights led to the concept of density scaling [15–18]. By introducing a generalized variable TV^γ, accounting for combined thermal and density effects, it was possible to superimpose isobaric and isothermal structural relaxation (τ_α) or viscosity (η) data for a given system into a single scaling curve, $\log(\tau_\alpha \text{ or } \eta) = f(TV^\gamma)$, where T and V are temperature and volume, respectively. The scaling exponent, γ, is a key parameter considered an alternative measure of the relative contributions of thermal and density effects. It follows directly from the relationship between the ratio E_V/E_P and γ, $(E_V/E_P) = [1/(1+\alpha_P T_g\gamma)]$, derived in Ref. [15] The equivalence between E_V/E_P and γ becomes obvious when noting that the term $\alpha_P T_g$ (where T_g is the liquid-glass transition temperature and α_P denotes the isobaric thermal expansion coefficient) varies only slightly for different glass-forming liquids [13,19]. The approximate constancy of the $\alpha_P T_g$ product for polymers is known as the empirical Boyer-Spencer rule [20], or the Bondi rule ($\alpha_P T_g \sim 0.16$) [21].

Further progress in understanding the density scaling concept has been achieved through molecular dynamics (MD), simulations pioneered by Dyre's group [22–24].

They performed MD simulations of spherical particles using generalized Lennard-Jones (LJ) potential, $U_{\mathrm{LJ}}(r) = C_r r^{-m} - C_t r^{-n}$, for modeling intermolecular interactions and demonstrating that generalized LJ potential can be well approximated by the effective potential inverse power, $U_{\mathrm{eff}}(r) = A_r r^{-m_{\mathrm{IPL}}} - A_t$, when small enough intermolecular distances are considered. Shortly afterward, Coslovich and Roland pointed out that the exponent m_{IPL} can be related to the scaling exponent γ, i.e., $m_{\mathrm{IPL}} = 3\gamma$ [25,26]. Thus, the magnitude of γ is determined by the steepness of the repulsive part of the intermolecular potential. Consequently, the data obtained from macroscopic experiments analyzed in terms of the density scaling can gain knowledge about the characteristics of intermolecular potential.

For experimental determination of the γ exponent, both temperature and density behavior of the structural relaxation time or viscosity has to be known. In practice, two independent experiments are carried out. The first provides the temperature and pressure dependencies of the structural relaxation times, $\tau_\alpha(T, P)$, or viscosity, $\eta(T, P)$, while $V_{\mathrm{sp}}(T, P)$ data are obtained from the second experiment. These two datasets allow for determining $\tau_\alpha(T, V)$ or $\eta(T, V)$. However, the experimental procedure outlined above possesses some drawbacks. Only a few laboratories in the world are equipped with HPBDS and PVT setups. Furthermore, for $V_{\mathrm{sp}}(T, P)$ measurements, a confining-fluid-type PVT apparatus developed by Zoller [27] is usually employed. This limits the determination of the specific volume to temperatures above 293 K. Consequently, the low-T_g liquids require extensive extrapolation of the data, which may lead to uncertainty in the value of γ.

This Letter demonstrates that the scaling exponent can be determined from HPBDS alone. Here, we use a fact that one of the dielectric parameters, i.e., dielectric loss strength, $\Delta\varepsilon$, depends on both density and temperature. Consequently, an alternative scaling procedure was derived in terms of dielectric parameters. The new form of density scaling is verified for five glass-forming liquids of different chemical architectures, dipole moment, and various tendencies to intermolecular correlations, including hydrogen bond formation. We found that an alternative scaling law works properly for systems exhibiting a constant value of the Kirkwood factor (g_K) at isochronal conditions. On the other hand, the scaling is broken for systems exhibiting $g_K \neq$ const at given τ_α or η.

Following Kirkwood-Fröhlich's statistical mechanical theory of dielectrics, the dielectric loss strength is related to temperature, density (ρ), the permanent dipole moment of the molecule (μ), and correlation factor (g_K) [28–30]:

$$\Delta\varepsilon = \frac{\mu^2}{3\epsilon_0 k_B} F g_K \frac{\rho}{T}, \tag{1}$$

where F is the local field correction factor, $\in_0$ denotes the vacuum permittivity, and k_B is the Boltzmann constant. According to the prediction made in Ref. [31] the term Fg_K in Eq. (1) should be isomorph invariant. It means that the Fg_K factor is expected to remain constant at isochronal or isoviscosity conditions. When true, the new form of the density scaling rule can be established as

$$\log(\tau_\alpha) = u[T(\Delta\varepsilon T)^{-\gamma}]. \tag{2}$$

The form of Eq. (2) indicates that the structural relaxation times determined from BDS measurements at different temperature-pressure thermodynamic states can be mapped onto the single scaling curve if plotted vs a new variable: $T(\Delta\varepsilon T)^{-\gamma}$. To determine the value of γ, only isobaric and isothermal dielectric measurements are required. On the other hand, there is no need to measure $V_{\mathrm{sp}}(T, P)$ anymore. In practice, the determination of γ is limited to the analysis of $\log(\Delta\varepsilon)$ vs $\log(T)$ at constant τ_α. Specifically, at isochronal conditions, $\log(\Delta\varepsilon)$ vs log(T) dependence is linear, with the correlation coefficient equal to $[(1-\gamma)/\gamma]$. The only experimental condition that must be satisfied is high accuracy in determining the dielectric strength value. If a typical parallel plate capacitor with Teflon spacer is used for dielectric studies, the gap between plates can slightly change during compression bringing an uncontrolled variation in the capacitor geometry and, thus, affecting $\Delta\varepsilon(T, P)$. To eliminate this undesirable effect, here we used interdigitated electrodes (IDE) (Micrux Technologies, Oviedo, Spain) presented in the left panel of Fig. 1. More experimental details are included in the Supplemental Material [32].

To validate the scaling formula expressed by Eq. (2), we performed isobaric and isothermal dielectric measurements of six glass-forming liquids: three van der Waals systems *N*, *N*-diethyl-meta-toluamide (DEET), triethyl-2-acetylcitrate (TEAC), and 4-vinyl-1,3-dioxolan-2-one (VPC) and three H-bonding liquids: glycerol, 2-ethyl-1-hexanol (2E1H) and 4-(hydroxymethyl)-1,3-dioxolan-2-one (H-PC). The structures of the studied compounds are depicted in the Supplemental Material [32]. VPC and H-PC are similar to propylene carbonate (PC), which was supposed to reveal the antiparallel ordering of molecules [33]. Compared to PC, VPC has the advantage of a 14 K higher T_g ($T_g = 171$ K) and does not crystallize in dielectric measurements. Furthermore, due to the same structure of the five-atom dioxolane ring, VPC and PC have a comparable permanent dipole moment $\mu = 5.0$ D, and thus the value of a static dielectric constant (ε_s). At the same time, due to the OH group located at the end of the alkyl tail, H-PC reveals a tendency to H-bond formation. Among the associated liquids, the canonical glass-former glycerin ($\mu = 2.67$ [34]) and monohydroxy alcohol 2-ethyl-1-hexanol have also been tested. In addition, TEAC with branched acetyl citrate chains and DEET with aromatic ring

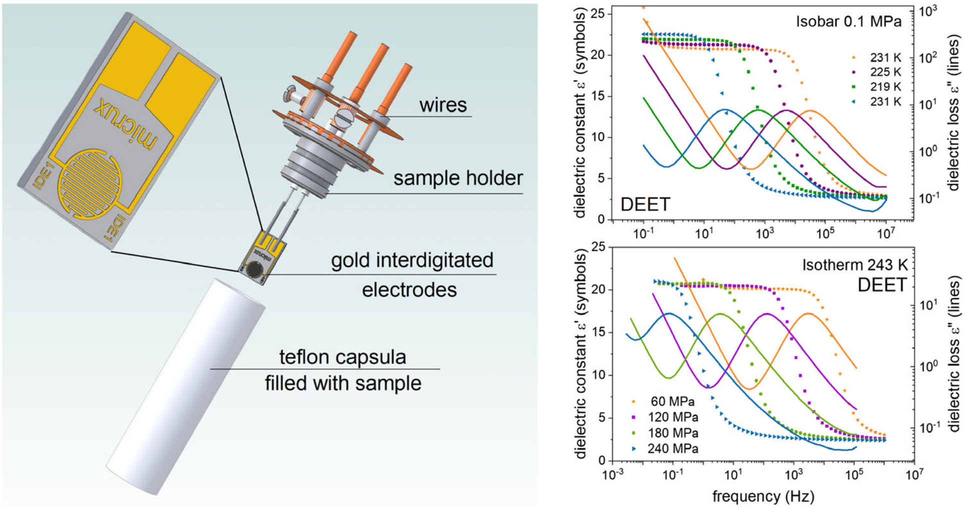

FIG. 1. Left panel: interdigitated electrodes connected to the sample holder. Right panel: dielectric spectra of DEET collected with the use of IDE.

have been examined. The value of μ and, thus $\Delta\varepsilon$ of TEAC and DEET are comparable ($\mu^{\mathrm{TEAC}} = 3.2$ vs $\mu^{\mathrm{DEET}} = 3.4$); however, for the latter one, an enhancement of static orientation correlations at lower temperatures has been found [35].

The representative dielectric spectra collected on cooling and compression are presented in the right panel of Fig. 1. As the temperature decreases at constant pressure, the dielectric loss curves of DEET move toward lower frequencies. Analogous behavior of dielectric loss $\varepsilon''(f)$ spectra is observed in the case of an isothermal compression. This indicates that the structural relaxation of DEET becomes slower during the cooling or compression, which is typical behavior also observed for other examined herein systems. The frequency corresponding to the α-peak maximum, $f_{\max}$, gives the value of the structural relaxation time, $\tau_\alpha = 1/2\pi f_{\max}$. The second quantity of interest is the strength of dielectric relaxation, $\Delta\varepsilon$. It can be extracted directly from the real part of complex dielectric permittivity $\varepsilon'(f)$ as the difference between two dielectric parameters: ε_s and ε_∞. The first denotes the value of permittivity ε' when the frequency goes to zero, while the latter ε_∞ (infinity) is determined from the high-frequency limit of $\varepsilon'(f)$. Herein, it should be emphasized that for polar materials with relatively high dielectric strength, the contribution of ε_∞ to $\Delta\varepsilon$ at given T, P conditions is minimal. Consequently, the temperature and pressure behavior of $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ can be successfully replaced by $\varepsilon_s(T,P)$ dependence. At the same time, $\Delta\varepsilon$ needs to be carefully determined for weekly polar materials since the temperature and pressure evolution of ε_∞ might substantially change $\Delta\varepsilon(T,P)$ behavior.

Having determined τ_α and $\Delta\varepsilon$ we are now ready to test the density scaling rule expressed by Eq. (2). As a starting point, we plot $\log\tau_\alpha$ against $\Delta\varepsilon$ along the isobar and isotherms for all tested herein glass formers [see Figs. 2(a) and 2(b)]. Note that in this procedure, the exact pressure value can stay unknown. Based on these data, one can plot $\log(\Delta\varepsilon)$ vs $\log(T)$ at isochronal conditions, as displayed in the left-side inset in Fig. 2. A linear fit to these data gives the value of the scaling exponent γ. Note that $\log(\Delta\varepsilon)$ vs $\log(T)$ of glycerol is a linear dependence almost parallel to X-axis, and therefore it has not been shown. Finally, we replotted the data from Fig. 2 by using the new scaling variable: $T(\Delta\varepsilon_s T)^{-\gamma}$. From the right-side inset to Fig. 2, it becomes obvious that five of six examined materials satisfy the prediction of Eq. (2), i.e., all collected data points fall onto a single curve. An exception of VPC will be discussed below. To check if the obtained value of γ is the same as the exponent in the original scaling law, we also plot the $\log\tau_\alpha$ of glycerol, 2E1H, H-PC, DEET, TEAC, and VPC using $f(TV^\gamma)$. The scaling procedure is presented in Fig. S3 [32] with the data of TEAC as an example. From Fig. 3, it becomes clear that the same value of γ exponent can be used to scale the relaxation times as a function of $f(TV^\gamma)$ and $T(\Delta\varepsilon T)^{-\gamma}$. It all implies that the term Fg_K in Eq. (1) is indeed isomorph invariant for five of the six examined materials. Note that, for H-bonding systems, i.e., glycerol, 2E1H, and H-PC, the TV^γ scaling works only in a pressure range limited to 350 MPa.

Equivalence between the scaling laws expressed by TV^γ and Eq. (2) was confirmed for five molecular liquids of different polarity, architecture, and ability to H-bond formation. However, for VPC, a global fitting analysis of isochronal $\log(\Delta\varepsilon)$ vs $\log(T)$ dependences using a linear function with one sharing parameter defining the slope does not match well with all data points. Furthermore, the determined value of γ equal to 1.23 is pretty surprising since the γ values close to unity are typical for ionic or hydrogen-bonded liquids but not for van der Waals

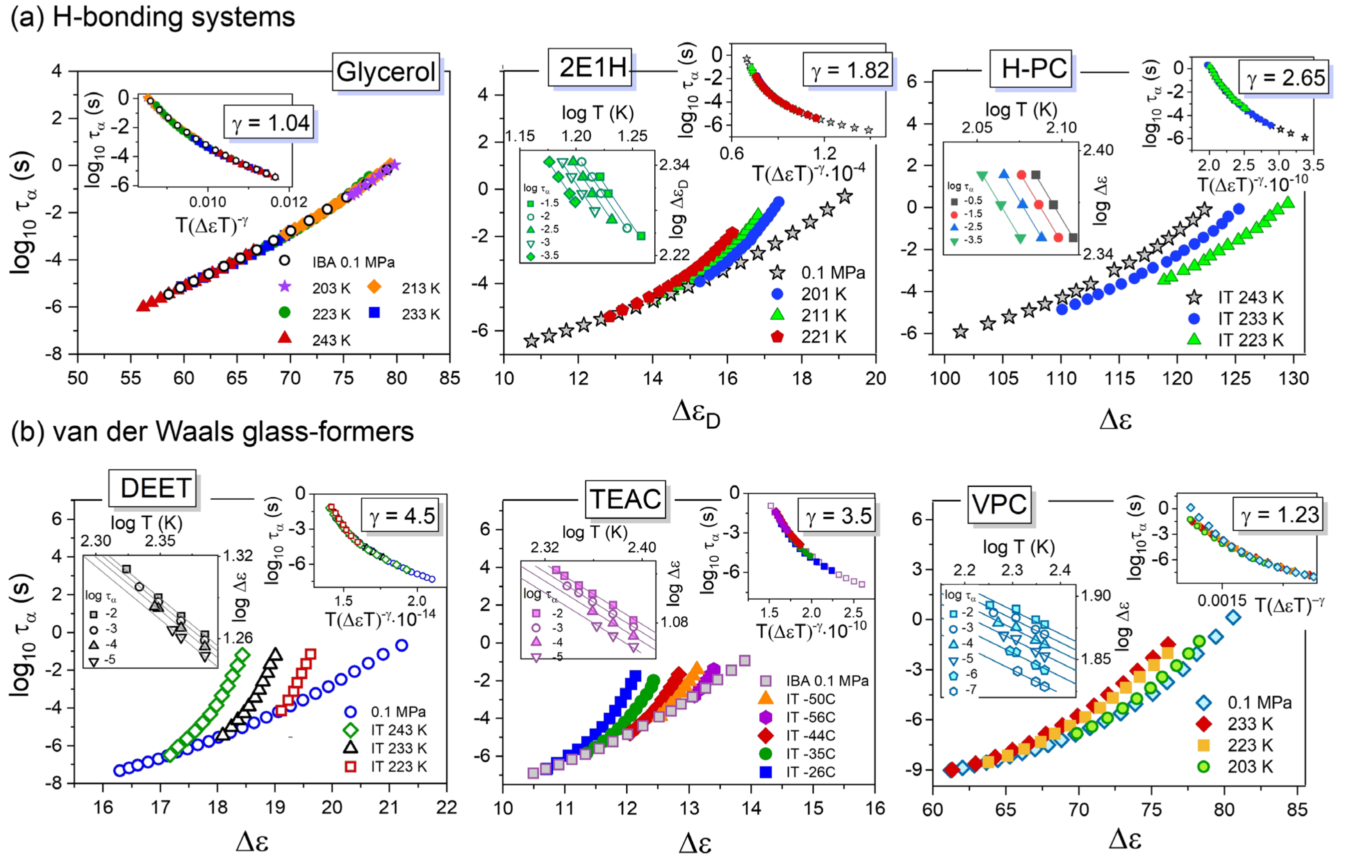

FIG. 2. Dielectric relaxation times of various H-bonding (a) and van der Waals (b) systems as a function of relaxation strength. Note that for 2E1H dielectric strength of the Debye process has been analyzed. Right insets: $\log \tau_\alpha$ vs scaling factor $T(\Delta\varepsilon_s T)^{-\gamma}$. Left inset: $\log \Delta\varepsilon$ vs log T determined from $\log \tau_\alpha(\Delta\varepsilon)$ plot at isochronal conditions.

systems. Additionally, one cannot achieve the satisfactory $T(\Delta\varepsilon_s T)^{-\gamma}$ scaling using this γ [see right-side inset to Fig. 2(b)]. Contrary, in TV^γ scaling, $\log \tau_\alpha$ of VPC superpose perfectly to a single curve, however, with the scaling exponent much higher and equal to 3.5 (see Fig. 3). This value is reasonable because it is very close to $\gamma = 3.7$ determined for structurally similar propylene carbonate [13]. All these discrepancies lead to the conclusion that the term Fg_K is no longer invariant for VPC.

To rationalize the obtained results, we calculated the Kirkwood factor at various T and P conditions for all six investigated materials, $g_K = (9k\varepsilon_0 M_{\mathrm{mol}} T / N_A \rho \mu^2)\,[(\varepsilon_s - \varepsilon_\infty) \times (2\varepsilon_s + \varepsilon_\infty)/\varepsilon_s(\varepsilon_\infty + 2)^2]$, where k is Boltzmann's constant, M_{mol} the molar weight, $\varepsilon_0 = 8.85 \times 10^{-12}\ \mathrm{C^2\,J^{-1}\,m^{-1}}$, N_A Avogadro number, ρ density, μ the molecular dipole moment. ε_s and ε_∞ denote the static and high-frequency dielectric permittivity, respectively. The importance of g_K has been highlighted many times experimentally [39,40] and theoretically [41,42]. The obtained temperature dependences of g_K are presented in Fig. 4(a). As can be seen, for all systems, instead of VPC g_K increases with

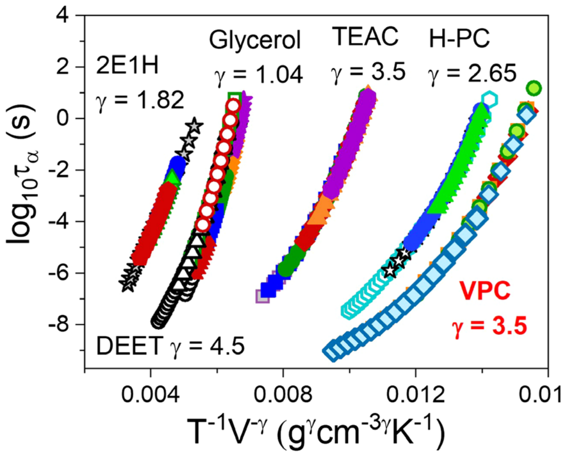

FIG. 3. Isothermal and isobaric dielectric relaxation times of examined systems as a function of scaling factor $T^{-1}V^{-\gamma}$. The PVT data of VPC and H-PC required for $T^{-1}V^{-\gamma}$ scaling are presented in Supplemental Material [32]. The EOS describing $V_{\mathrm{sp}}(T,P)$ data of glycerol, 2E1H, DEET, and TEAC, necessary to obtain $T^{-1}V^{-\gamma}$ scaling, were taken from Refs. [36–38].

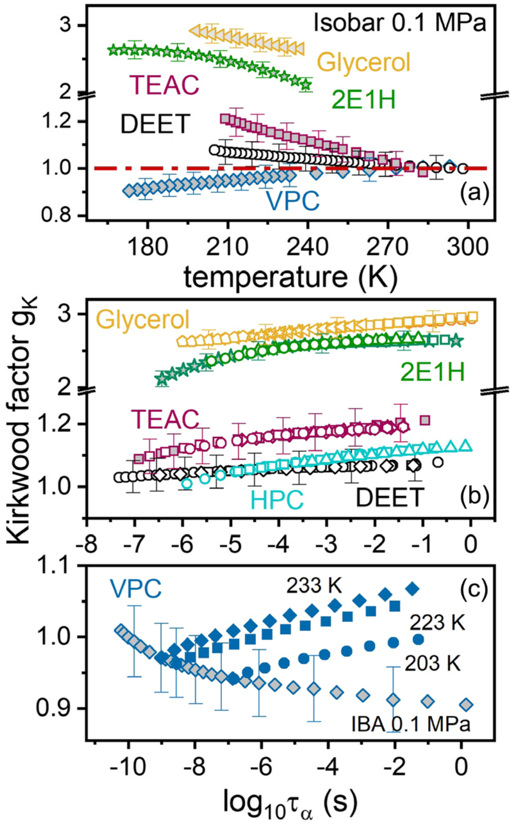

FIG. 4. (a) The temperature dependence of g_K. (b) The g_K of examined systems along the isotherms and isobar plotted as a function of relaxation times. (c) The g_K of VPC along the isotherms and isobar plotted as a function of relaxation times. 5% error bars are included. The temperature and pressure dependences of density used to determine g_K were taken from the equation of state available in the literature and presented in Supplemental Material [32].

decreasing temperature and takes the value above unity near T_g. Since $g_K > 1$, parallel orientations of permanent dipoles seem to be preferred in these cases. Obviously, glycerol and 2E1H have the highest g_K due to strong H-bond interactions between the molecules. At the same time, cooling of VPC brings a decrease in the g_K from unity at room temperature to 0.9 close to T_g, thereby indicating antiparallel alignment of dipoles in this glass former. Note that the tendency to anti-parallel ordering of VPC could be deduced directly from comparing the dielectric strength of VPC and H-PC. Namely, despite the slightly lower dipole moment (see Supplemental Material [32]), the latter is characterized by a markedly higher value of $\Delta\varepsilon$ (82 vs 130 close to T_g). In this context, the question arises whether the isobaric cooling and isothermal compression bring a similar change in g_K? To address this issue, we plotted g_K as a function of structural relaxation time along the isobar and isotherms. As presented in Fig. 4(b), for DEET, TEAC, H-PC, 2E1H, and glycerol, we found that the data collapsed quite well onto a single curve, indicating that the factor g_K alone is constant at a given timescale of structural relaxation. Thus, it is not surprising that the structural relaxation times of these materials obey both scaling laws with a typical value of scaling exponent. A completely different scenario is observed for the last sample, VPC. Specifically, isobaric and isothermal g_K data have different trends. While cooling of VPC brings a decrease in g_K, isothermal compression leads to an increase in the value of g_K. Consequently, the g_K factor is no more isomorph invariant and gives a different contribution to the value of $\Delta\varepsilon$ [Eq. (1)], making the use of dielectric strength to determine the γ exponent impossible. Generally, this is the first time when temperature and pressure behavior of g_K has been thoroughly analyzed. Therefore, it would be interesting to verify in the future whether the different temperature and pressure dependence of g_K is a general behavior for molecules with preferred antiparallel ordering or if it is only a special case for VPC.

In summary, the analysis of isothermal and isobaric dependences of structural relaxation times and dielectric strength $\Delta\varepsilon$ obtained in dielectric measurements gives a unique possibility to determine the scaling exponent γ accounting for thermal and density effects governing relaxation dynamics. By introducing a new variable: $T(\Delta\varepsilon T)^{-\gamma}$ we successfully scaled the structural relaxation times of simple van der Waals liquids and H-bonding materials, including canonical glass-former glycerol. Notably, the value of the scaling exponent γ is precisely the same as that obtained in the original TV^γ density scaling rule. This finding opens the possibility to determine the values of γ for structurally diverse glass-forming liquids, thereby leading to a better understanding of the dynamics of viscous fluids and the glass transition. However, one should note that the proposed approach is suitable if the Kirkwood factor (g_K) is an isomorph-invariant quantity and does not work when the isothermal compression and isobaric cooling bring about different effects on g_K (as found for a derivative of propylene carbonate). This finding initiates another question that needs to be answered in the future, whether the preferred antiparallel ordering or molecules in a supercooled state is manifested by different temperature and pressure dependence of g_K.

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