THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

pubs.acs.org/JPCL Letter

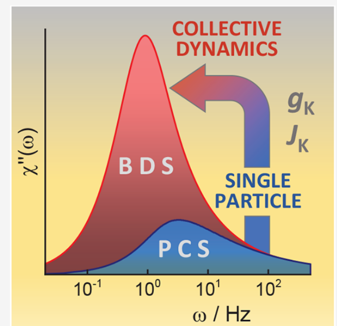
From Single-Particle to Collective Dynamics in Supercooled Liquids

Dmitry V. Matyushov* and Ranko Richert*

Cite This: J. Phys. Chem. Lett. 2023, 14, 4886−4891 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: It has been recognized recently that the considerable difference between photon correlation (PCS) and dielectric (BDS) susceptibility spectra arises from their respective association with single-particle and collective dynamics. This work presents a model that captures the narrower width and shifted peak position of collective dynamics (BDS), given the single-particle susceptibility derived from PCS studies. Only one adjustable parameter is required to connect the spectra of collective and single-particle dynamics. This constant accounts for cross-correlations between molecular angular velocities and the ratio of the first- and second-rank single-particle relaxation times. The model is tested for three supercooled liquids, glycerol, propylene glycol, and tributyl phosphate, and is shown to provide a good account of the difference between BDS and PCS spectra. Because PCS spectra appear to be rather universal across a range of supercooled liquids, this model provides a first step toward rationalizing the more material-specific dielectric loss profiles.



The dynamics of supercooled liquids has been the subject of intense research for over a century. Common observations regarding these glass-forming liquids are their super-Arrhenius temperature dependence of viscosity and relaxation time constants as well as the non-exponential decay correlation of the corresponding time correlation functions associated with structural relaxation, equivalent to asymmetrically broadened susceptibility profiles in the frequency domain.[1] However, the extent of broadening and shape of these profiles are material-specific, which complicates a unified description of structural relaxation in viscous materials.

A common experimental approach to the dynamics of supercooled liquids is by broadband dielectric spectroscopy (BDS), providing access to the permittivity $\tilde{\varepsilon}(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega)$, also denoted $\varepsilon^*(\omega)$.[2] The widths of such dielectric loss spectra, $\varepsilon''(\omega)$, vary with the temperature and are material-specific even if compared at a common loss peak frequency (ω_{max}) or average relaxation time. In fact, a recent study has shown that the loss peak width near the glass transition temperature, T_g, narrows systematically with an increasing dielectric constant, ε_s.[3] This feature is not observed in all experimental approaches to the dynamics of structural relaxation. Recent experiments have demonstrated that the susceptibility spectra, $\chi''(\omega)$, derived from photon correlation spectroscopy (PCS) display a rather universal appearance, even across those liquids for which the dielectric $\varepsilon''(\omega)$ profiles vary considerably.[4] For frequencies not too far from ω_{max}, the PCS results can be approximated by a Cole−Davidson-type function, $\chi''(\omega) \propto \mathrm{Im}[(1 - i\omega\tau_{CD})^{-\gamma}]$, with $\gamma \approx 0.5$.

The two experimental approaches to rotational dynamics differ in the rank of the reported relaxation time: BDS reports the dynamics of the first-order Legendre polynomial $\langle P_1(\hat{\mathbf{u}}\cdot\hat{\mathbf{e}})\rangle$ for the projection of the unit dipole vector $\hat{\mathbf{u}}$ on the field direction $\hat{\mathbf{e}}$ versus the second-order Legendre polynomial $\langle P_2(\hat{\mathbf{u}}\cdot\hat{\mathbf{e}})\rangle$ reported by PCS. Because rotation in viscous liquids involves large jump angles,[5] the ratio $\kappa = \tau_s^{(1)}/\tau_s^{(2)}$ of first-rank, $\tau_s^{(1)}$, to second-rank, $\tau_s^{(2)}$, rotational relaxation times falls below the diffusive limit of $\kappa = 3$, reaching the value of $\kappa \simeq 1.57$ for large-amplitude rotational jumps.[6] The more significant and qualitative difference between $\chi''_{PCS}(\omega)$ and $\varepsilon''_{BDS}(\omega)$ has been rationalized by the PCS technique being mostly sensitive to single-particle dynamics, whereas $\tilde{\varepsilon}(\omega)$ derived from the BDS approach is associated with collective dynamics.[7,8] As may be expected, the difference between PCS and BDS spectral shapes disappears for weakly polar liquids (dielectric increment of $\lesssim 0.2$).[4]

On the basis of approximations detailed below, Keyes[9] derived the relation

$$\tau_M = g_K \tau_s \tag{1}$$

which connects the average collective relaxation time, τ_M, of the macroscopic dipole moment **M** to its single-particle counterpart, $\tau_s = \tau_s^{(1)}$, via the Kirkwood correlation factor g_K. Comparing τ_M from BDS to $\tau_s^{(2)}$ from PCS reveals that the ratio $\tau_M/\tau_s^{(2)}$ near T_g exceeds g_K by far, assuming values of up to 20 reported for propylene glycol.[10] Moreover, the temperature dependence of

Received: April 9, 2023
Accepted: May 10, 2023

https://doi.org/10.1021/acs.jpclett.3c00959
J. Phys. Chem. Lett. 2023, 14, 4886−4891

τ_M and $\tau_s^{(2)}$ differs by more than can be explained by $g_K(T)$ alone. Therefore, Keyes's approximation in eq 1 does not correctly capture the difference between collective and single-particle dynamics in viscous liquids.

In an extension of Keyes's approach, Kivelson and Madden added a dynamical correlation parameter[11,12] J_K, resulting in the Keyes−Kivelson−Madden (KKM) relation[9,13−15]

$$\tau_M = (g_K/J_K)\tau_s = (g_K/J_K)\kappa\tau_s^{(2)} \tag{2}$$

The dynamical correction parameter J_K is often found to be close to unity for high-temperature liquids,[12,16−19] thus yielding the simplified result of eq 1. However, we show below that adopting $J_K/\kappa \neq 1$ is essential for translating single-particle into collective loss spectra, i.e., $\chi''_{PCS}(\omega) \to \varepsilon''_{BDS}(\omega)$, which is the aim of the present work. Calculations based on experimental PCS spectra will then be shown to compare favorably to measured BDS loss profiles. Moreover, experimental evidence shows larger separations between single-particle and collective relaxation times at lower temperatures, consistent with J_K/κ decreasing with reducing the temperature.

The dielectric function for polar materials with $\tilde{\varepsilon}(\omega) \gg \varepsilon_\infty$ is determined by the equation[20,21]

$$\tilde{\varepsilon}(\omega) - \varepsilon_\infty = \Delta\varepsilon[1 + i\omega\tilde{\phi}_M(\omega)] \tag{3}$$

where $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the dielectric increment, i.e., the difference between low- and high-frequency limits of permittivity. Functions with tildes are used to denote Laplace−Fourier transforms of time correlation functions[22]

$$\tilde{\phi}_a(\omega) = \int_0^\infty dt e^{i\omega t}\phi_a(t) \tag{4}$$

where a = M and s specifies either the normalized time autocorrelation function of the total dipole moment $\mathbf{M}(t)$ (a = M) or single-particle dipole orientations (a = s; see below). The dipole moment autocorrelation function entering eq 3 is given as

$$\phi_M(t) = \frac{\langle \mathbf{M}(t)\cdot\mathbf{M}\rangle}{\langle \mathbf{M}\cdot\mathbf{M}\rangle} \tag{5}$$

Here, the angular brackets denote an equilibrium ensemble average, and the deviation from the average dipole $\delta\mathbf{M}(t) = \mathbf{M}(t) - \langle\mathbf{M}\rangle$ is dropped in eq 5, given that $\langle\mathbf{M}\rangle = 0$ in an isotropic material. Equation 5 also utilizes the notation $\mathbf{M}(0) = \mathbf{M}$, and we do not specify $t = 0$ for all dynamic variables used below; e.g., $A(0) = A$. The time correlation function allows one to define the average (integral) relaxation times in eqs 1 and 2

$$\tau_a = \int_0^\infty dt\phi_a(t) \tag{6}$$

with a = M and s. For both cases, τ_M and τ_s, this relaxation time is the $\omega = 0$ value of the corresponding $\tilde{\phi}_a(\omega)$ of eq 4.

The rotational relaxation time of a single dipole in the liquid is associated with the time autocorrelation function of the molecular dipole moment $\boldsymbol{\mu}(t)$. By defining the unit vector specifying the dipole orientation $\hat{\mathbf{u}}(t) = \boldsymbol{\mu}(t)/\mu$, one obtains

$$\phi_s(t) = \langle \hat{\mathbf{u}}(t)\cdot\hat{\mathbf{u}}\rangle \tag{7}$$

The average (integral) single-particle relaxation time in eqs 1 and 2 follows from the time integral of $\phi_s(t)$ in eq 6, for which $\tau_s = \tilde{\phi}_s(0)$ holds.

To build a connection between the correlation functions $\phi_M(t)$ and $\phi_s(t)$, we make use of the corresponding memory functions. The time correlation functions $\phi_a(t)$, where a = M and s, satisfy the memory equation[23] with the memory function $K_a(t)$

$$\dot{\phi}_a(t) + \int_0^t d\tau K_a(t-\tau)\phi_a(\tau) = 0 \tag{8}$$

These memory functions describe the dynamics of local, microscopic interactions (collisions in the gas phase), which add up through the time convolution integral in eq 8 to produce the dynamics represented by the time correlation function. The memory integral equation becomes a linear algebraic equation upon Laplace−Fourier transform

$$\tilde{\phi}_a(\omega) = [-i\omega + \tilde{K}_a(\omega)]^{-1} \tag{9}$$

The time-domain memory functions satisfy the following equations:[19,23]

$$K_M(t) = \frac{\langle \dot{\mathbf{M}}\cdot\dot{\mathbf{M}}\rangle}{\langle \mathbf{M}\cdot\mathbf{M}\rangle} f_M(t) \tag{10}$$

and

$$K_s(t) = \langle \dot{\hat{\mathbf{u}}}\cdot\dot{\hat{\mathbf{u}}}\rangle f_s(t) \tag{11}$$

where $\langle \dot{\hat{\mathbf{u}}}\cdot\dot{\hat{\mathbf{u}}}\rangle = \omega_s^2 = -\ddot{\phi}_s(0)$. The normalized functions $f_M(t)$ and $f_s(t)$ with $f_M(0) = f_s(0) = 1$ are the time-dependent components of the corresponding memory functions. The variance of the sample dipole moment $\langle\mathbf{M}\cdot\mathbf{M}\rangle = g_K\mu^2 N$ in the denominator in eq 10 is the product of the squared molecular dipole μ, the number of dipoles N in the sample, and the Kirkwood factor

$$g_K = 1 + \sum_{i\neq 1}\langle \hat{\mathbf{u}}_1\cdot\hat{\mathbf{u}}_i\rangle \tag{12}$$

where $\hat{\mathbf{u}}_i$ is the unit directional vector of dipole moment i.

The variance of the time derivative of the sample dipole moment in the numerator of eq 10 becomes

$$\langle \dot{\mathbf{M}}\cdot\dot{\mathbf{M}}\rangle = N\mu^2\omega_s^2 J \tag{13}$$

where the angular velocity cross-correlations vanish in the canonical ensemble, i.e.,

$$J = 1 + \omega_s^{-2}\sum_{i\neq 1}\langle \dot{\hat{\mathbf{u}}}_1\cdot\dot{\hat{\mathbf{u}}}_i\rangle = 1 \tag{14}$$

Combining these results in eq 10, one obtains

$$K_M(t) = \frac{\omega_s^2}{g_K} f_M(t) \tag{15}$$

In contrast to J in eq 14, the dynamic correlation factor in the KKM equation does not reduce to a trivial value. It is given as[11,14] (see the Supporting Information for derivation)

$$J_K = 1 + \frac{\int_0^\infty dt\psi_c(t)}{\int_0^\infty dt\psi_s(t)} \tag{16}$$

where $\psi_c(t)$ describes cross-correlations of angular rotational velocities of distinct molecules

$$\psi_c(t) = \sum_{i\neq 1}\langle \dot{\hat{\mathbf{u}}}_1\cdot\dot{\hat{\mathbf{u}}}_i(t)\rangle^\dagger \tag{17}$$

https://doi.org/10.1021/acs.jpclett.3c00959
J. Phys. Chem. Lett. 2023, 14, 4886−4891

Here, $\langle ... \rangle^\dagger$ denotes the correlation function propagated in the orthogonal space of Mori's[24] projection operator technique,[23,25] $\langle \dot{\hat{\mathbf{u}}}_1 \cdot \dot{\hat{\mathbf{u}}}_i(t) \rangle^\dagger = \langle \dot{\hat{\mathbf{u}}}_1 \cdot \mathrm{e}^{i(1-\hat{P})\mathcal{L}t} \dot{\hat{\mathbf{u}}}_i \rangle$, with $\mathcal{L}$ being the Liouville operator and $\hat{P}$ being the projection operator. In contrast, $\psi_s(t)$ is the single-particle correlation function of angular velocities

$$\psi_s(t) = \langle \dot{\hat{\mathbf{u}}} \cdot \dot{\hat{\mathbf{u}}}(t) \rangle^\dagger \tag{18}$$

satisfying the initial condition $\psi_s(0) = \omega_s^2 = 2k_B T/I$ for a symmetric top with the moment of inertia I.

The derivation thus far does not involve any approximations and can be viewed as the definition of the unknown time-dependent functions $f_M(t)$ and $f_s(t)$. Given that they specify the time decay of the corresponding memory functions, they are expected to relax faster[23,26] than the respective correlation functions, $\phi_M(t)$ and $\phi_s(t)$. Following Keyes,[9] one can adopt a simple approximation assuming that the integral relaxation times of the memory functions $K_M(t)$ and $K_s(t)$ are equal to a common value τ_K, which implies

$$\tau_K = \tilde{f}_M(0) = \tilde{f}_s(0) \tag{19}$$

This approximation, used for the $\omega = 0$ limit in eq 9, leads to eq 1.

In what follows, the constraint of eq 19 will be dropped, thus allowing for distinct integral relaxation times of the two memory functions, $K_M(t)$ and $K_s(t)$. Equation 19 puts a single-value constraint on the $\omega = 0$ values of $\tilde{f}_M(\omega)$ and $\tilde{f}_s(\omega)$ but does not specify these two functions. An approximation consistent with the first relation in eq 2 is to assume $\tilde{f}_M(\omega) = J_K \tilde{f}_s(\omega)$. This approximation leads to the following connection between the memory functions

$$\tilde{K}_M(\omega) = (g_K/J_K)^{-1} \tilde{K}_s(\omega) \tag{20}$$

To account for the second rank of PCS, we replace the retardation parameter g_K/J_K with ζ_K that follows from the second KKM relation in eq 2

$$\zeta_K = (g_K/J_K)\kappa \tag{21}$$

Given that $\tilde{\phi}_M(\omega)$ and $\tilde{\phi}_s(\omega)$ are now related through the corresponding $\tilde{f}_a(\omega)$ functions, one obtains the equation for the dielectric permittivity $\tilde{\varepsilon}(\omega)$ in terms of the single-particle correlation function $\tilde{\phi}_s(\omega)$ and the retardation parameter ζ_K

$$\frac{\tilde{\varepsilon}(\omega) - \varepsilon_s}{\Delta\varepsilon} = \frac{i\omega\zeta_K}{i\omega(1-\zeta_K) + \tilde{\phi}_s^{-1}(\omega)} \tag{22}$$

We note that simple proportionality between $\tilde{f}_M(\omega)$ and $\tilde{f}_s(\omega)$ cannot be correct in the whole range of frequencies because it would violate the normalization condition $f_M(0) = f_s(0) = 1$ upon inverse Laplace–Fourier transform. It should instead be viewed as an approximation applied to the range of frequencies near the peaks of dielectric and single-particle loss spectra. For instance, if $\tilde{f}_M(\omega)$ and $\tilde{f}_s(\omega)$ are Debye functions with the relaxation times τ_K^a, one would anticipate $\tau_K^M = J_K\tau_K^s = J_K\kappa\tau_K^{s,(2)}$ and $\tau_K^a\omega \ll 1$ in the frequency range applicable to experimental conditions. Both static and dynamic cross-correlations affect the relation between the single-particle and collective dynamics, but they can both be reduced to numerical scaling factors at sufficiently small peak frequencies characteristic of low-temperature (supercooled) liquids.

The single-particle autocorrelation function $\tilde{\phi}_s(\omega)$ can be related to experimental data reporting the imaginary part of the susceptibility function $\tilde{\chi}_s(\omega)$ derived from PCS measurements, with the connection between the two functions being provided by the standard Kubo linear response formalism.[23] Note that, like the single-particle autocorrelation function $\phi_s(t)$, the response function $\chi_s(t)$ is normalized by the condition $\chi_s(0) = 1$. This condition is typically not met by experimental data reporting $\chi_s''(\omega)$ spectra in arbitrary units. In the calculations presented here, $\chi_s''(\omega)$ was fitted to a linear combination of Debye functions with the requirement of the relaxation amplitudes summing up to unity

$$\chi_s''(\omega) = \sum_i a_i \frac{\omega\tau_i}{1 + \omega^2\tau_i^2}, \quad \sum_i a_i = 1 \tag{23}$$

With the employment of eq 23 for fitting the experimental result, Kubo's relation[23]

$$\tilde{\chi}_s(\omega) = 1 + i\omega\tilde{\phi}_s(\omega) \tag{24}$$

was used to calculate $\tilde{\phi}_s(\omega)$. This function was used to produce $\tilde{\varepsilon}(\omega)$ in eq 22 by adopting the experimental values for $\Delta\varepsilon$.

This procedure was applied to generate $\tilde{\varepsilon}(\omega)$ curves for glycerol at T = 210 K (Figure 1), propylene glycol (PG) at T = 190 K (Figure 2), and tributyl phosphate (TBP) at T = 147 K (Figure 3) from corresponding loss spectra $\chi_s''(\omega)$. The Kirkwood factors for three liquids were calculated from Wertheim's theory[27,28] (Table 1; see the Supporting Information for more details). This mean-field theory calculates the condensed-phase molecular dipole moment μ' and molecular polarizability α' from the corresponding gas-phase values μ and α (Table 1). These two parameters are used to specify the effective mean-field polarity parameter

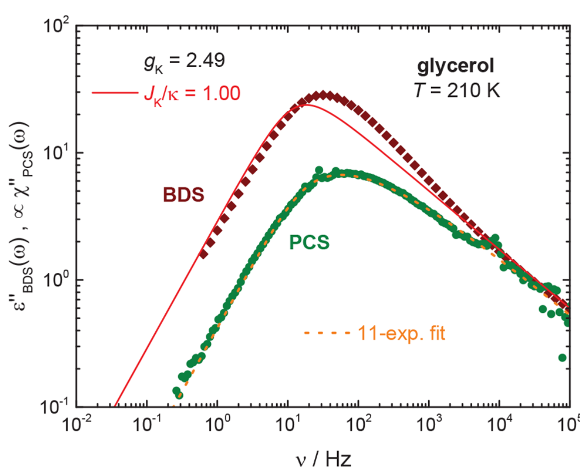


Figure 1. Experimental results for the dielectric loss spectrum $\varepsilon''(\omega)$ (BDS, diamonds) and the photon correlation susceptibility $\chi''(\omega)$ (PCS, circles) of glycerol at T = 210 K, taken from Gabriel et al.[10] The orange dotted line is a fit to the PCS data, and the red solid line is based on eq 22 with J_K/κ = 1.00, using g_K = 2.49 calculated from Wertheim's theory (Table 1).

https://doi.org/10.1021/acs.jpclett.3c00959
J. Phys. Chem. Lett. 2023, 14, 4886−4891

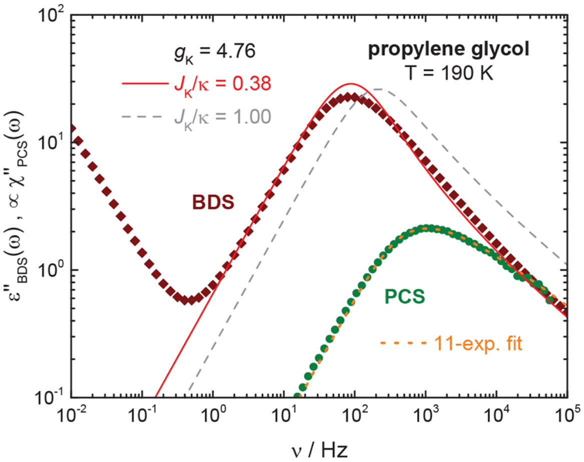


Figure 2. Experimental results for the dielectric loss spectrum $\varepsilon''(\omega)$ (BDS, diamonds) and the photon correlation susceptibility $\chi''(\omega)$ (PCS, circles) of propylene glycol at T = 190 K, taken from Böhmer et al.[29] The orange dotted line is a fit to the PCS data, and the gray dashed line and red solid line are based on eq 22 with J_K/κ = 1.00 and J_K/κ = 0.38, respectively, using g_K = 4.76 calculated from Wertheim's theory (Table 1).

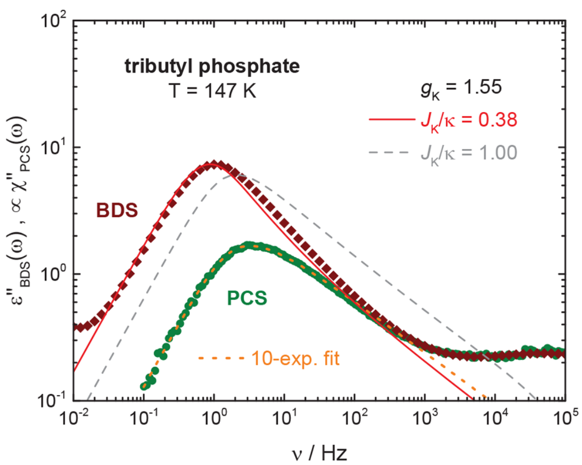


Figure 3. Experimental results for the dielectric loss spectrum $\varepsilon''(\omega)$ (BDS, diamonds) and the photon correlation susceptibility $\chi''(\omega)$ (PCS, circles) of tributyl phosphate at T = 147 K, taken from Pabst et al.[7] The orange dotted line is a fit to the PCS data, and the gray dashed line and red solid line are based on eq 22 with J_K/κ = 1.00 and J_K/κ = 0.38, respectively, using g_K = 1.55 calculated from Wertheim's theory (Table 1).

$$y_{eff} = (\rho/9\varepsilon_0)[(\mu')^2/(k_BT) + 3\alpha'] \qquad (25)$$

where ε_0 is the vacuum permittivity and ρ is the liquid number density. The polarity parameter enters the Kirkwood−Onsager equation[28]

$$(\varepsilon_s - 1)(2\varepsilon_s + 1) = 9y_{eff}\varepsilon_s g_K \qquad (26)$$

from which g_K is calculated.

The ratio J_K/κ in eqs 21 and 22 remains unspecified and was used to fit eq 22 to the experimental $\varepsilon''(\omega)$. The resulting values are listed in Table 1. The comparison between the theory and experiment regarding $\varepsilon''(\omega)$ in Figures 1−3 demonstrates that the present approach leads to a good account of the frequency-dependent collective dynamics based solely on the single-particle dynamics and a single constant ζ_K that contains the Kirkwood correlation factor g_K (eq 21). Uncertainties in the reported values of the liquid dipole moment, polarizability, and hard-sphere diameter might affect the calculation of g_K in Wertheim's formalism (see the Supporting Information). The theory, however, requires only ζ_K, and g_K is calculated here only to estimate J_K/κ. While data for only one temperature per material have been analyzed, studies comparing BDS and PCS spectra reveal that the relaxation time ratio τ_M/τ_s increases with a decreasing temperature. For instance, the value of τ_M/τ_s for propylene glycol increases by 50% when changing the temperature from T = 190 to 175 K.[29] This implies larger values for the memory function dynamic correlation factor J_K (eq 16) at higher temperatures, consistent with the notion of $J_K \approx 1$ in the fluid state.

The decades-long inquiry[9,13−15,26] addressed here in application to BDS of low-temperature liquids is the relation between the collective and single-particle dynamics in liquids. Collective relaxation is universally slowed down relative to single-particle dynamics, and the common wisdom[30] in the field suggests that collective dynamics, involving dynamic cross-correlations, are fundamentally distinct from single-particle dynamics. The simplified form of the KKM equation adopting J_K = 1 (eq 1) opposes this assessment. The limit J_K = 1 implies that slowing down of collective dynamics is achieved exclusively by accounting for local static correlations between the liquid dipoles in terms of the Kirkwood factor. A good performance of this assumption for liquids at normal (opposed to supercooled) conditions[12,16−19] supports this view. However, BDS of low-temperature liquids requires stronger retardation than given solely by the Kirkwood factor, and adopting $J_K/\kappa < 1$ is required (Figures 2 and 3). This simple extension has allowed us to convert the single-particle correlation function into the collective function by utilizing a single retardation parameter ζ_K (eq 21).

As mentioned above, a simple proportionality between frequency domain single-particle and collective memory functions can only hold in a limited range of frequencies. Development of practical functionalities for the single-particle memory function remains a challenge for the theory development. This function is directly related to the experimentally

Table 1. Liquid Parameters Used To Calculate $\tilde{\varepsilon}(\omega)$ from $\tilde{\phi}_s(\omega)$ and Kirkwood Factors g_K

liquid	T (K)	μ (D)	σ (Å)[a]	α (Å^3)	ρ (g/cm^3)	ε_∞	ε_s	μ' (D)[b]	g_K	J_K/κ[c]
glycerol	210	2.67	5.15	8.17	1.314	2.25	68.6	3.71	2.49	1.00
PG	190	2.0	5.12	8.81	0.998	2.17	63.7	2.55	4.76	0.38
TBP	147	2.9	7.97	27.6	1.114	2.23	20.0	3.76	1.55	0.38

[a]Hard-sphere diameter. [b]Calculated from Wertheim's theory (see the Supporting Information). [c]Adjusted as a fitting parameter.

https://doi.org/10.1021/acs.jpclett.3c00959
J. Phys. Chem. Lett. 2023, 14, 4886−4891

observable single-particle response function. One obtains by substituting eq 9 to eq 24

$$\tilde{\chi}_s(\omega) = [1 - i\omega\tilde{K}_s^{-1}(\omega)]^{-1} \quad (27)$$

It has been recently suggested that $\chi_s''(\omega)$ universally follows the scaling $\propto \omega^{-1/2}$ at large frequencies.[4,31] Such a scaling requires $\tilde{K}_s(\omega) \propto \omega^{1/2}$ in eq 27. This functionality, however, contradicts the interpretation[26] of normalized $K_s(t)$ as the characteristic function of the probability density $P(\omega)$

$$K_s(t) = K_s(0)\int_{-\infty}^{\infty} d\omega P(\omega) e^{-i\omega t} \quad (28)$$

The power spectrum $P(\omega) = (\pi K_s(0))^{-1}\tilde{K}_s'(\omega)$ is expected to produce an infinite sequence of spectral moments

$$\langle \omega^{2n} \rangle = \int_{-\infty}^{\infty} d\omega \omega^{2n} P(\omega) \quad (29)$$

It is obvious that $\tilde{K}_s(\omega) \propto \omega^{1/2}$ does not allow any frequency moments to exist and a more general functional form should be sought.

In summary, the aim of this work is to provide a rationale for the relation between collective (BDS) and single-particle (PCS) dynamics in supercooled liquids. Applying ideas from the KKM approach to the memory function formalism facilitates the calculation of the frequency-dependent collective dynamics from the single-particle susceptibility, thus going beyond a model that relates only the integral time constants. The approach is tested on the basis of BDS and PCS spectra reflecting the collective and single-particle dynamics, respectively. The theory provides a good account of the collective dynamics for three glass-forming materials, each based on two constants, the Kirkwood correlation factor g_K and an adjustable parameter J_K/κ (Table 1) that quantifies the retardation of the collective memory function $K_M(t)$ relative to its single-particle counterpart $K_s(t)$ and accounts for the different ranks of BDS and PCS relaxation times. This retardation effect is negligible for high-temperature fluids but becomes enhanced in viscous materials as the temperature is lowered toward the glass transition temperature T_g.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.3c00959.

Derivation of the KKM equation and properties of the liquids used in the analysis and calculations of their Kirkwood factors (PDF)

Transparent Peer Review report available (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Dmitry V. Matyushov − *School of Molecular Sciences and Department of Physics, Arizona State University, Tempe, Arizona 85287-1504, United States;* orcid.org/0000-0002-9352-764X; Email: dmitrym@asu.edu

Ranko Richert − *School of Molecular Sciences, Arizona State University, Tempe, Arizona 85287-1604, United States;* orcid.org/0000-0001-8503-3175; Email: ranko.richert@asu.edu

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpclett.3c00959

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the National Science Foundation under Grants CHE-2154465 (to Dmitry V. Matyushov) and DMR-1904601 (to Ranko Richert).

■ REFERENCES

(1) Angell, C. A.; Ngai, K. L.; McKenna, G. B.; McMillan, P. F.; Martin, S. W. Relaxation in glassforming liquids and amorphous solids. *J. Appl. Phys.* **2000**, *88*, 3113−3157.

(2) Richert, R. Supercooled liquids and glasses by dielectric relaxation spectroscopy. *Adv. Chem. Phys.* **2014**, *156*, 101−195.

(3) Paluch, M.; Knapik, J.; Wojnarowska, Z.; Grzybowski, A.; Ngai, K. L. Universal behavior of dielectric responses of glass formers: Role of dipole-dipole interactions. *Phys. Rev. Lett.* **2016**, *116*, 025702.

(4) Pabst, F.; Gabriel, J. P.; Böhmer, T.; Weigl, P.; Helbling, A.; Richter, T.; Zourchang, P.; Walther, T.; Blochowicz, T. Generic structural relaxation in supercooled liquids. *J. Phys. Chem. Lett.* **2021**, *12*, 3685−3690.

(5) Hinze, G. Geometry and time scale of the rotational dynamics in supercooled toluene. *Phys. Rev. E* **1998**, *57*, 2010−2018.

(6) Keyes, T. Theory of relative reorientational correlation times for first and second rank spherical harmonics. *J. Chem. Phys.* **1972**, *57*, 767−769.

(7) Pabst, F.; Helbling, A.; Gabriel, J.; Weigl, P.; Blochowicz, T. Dipole-dipole correlations and the Debye process in the dielectric response of nonassociating glass forming liquids. *Phys. Rev. E* **2020**, *102*, 010606.

(8) Körber, T.; Stäglich, R.; Gainaru, C.; Böhmer, R.; Rössler, E. A. Systematic differences in the relaxation stretching of polar molecular liquids probed by dielectric vs magnetic resonance and photon correlation spectroscopy. *J. Chem. Phys.* **2020**, *153*, 124510.

(9) Keyes, T. Microscopic theory of collective anisotropic molecular reorientation. *Mol. Phys.* **1972**, *23*, 737−743.

(10) Gabriel, J. P.; Zourchang, P.; Pabst, F.; Helbling, A.; Weigl, P.; Böhmer, T.; Blochowicz, T. Intermolecular cross-correlations in the dielectric response of glycerol. *Phys. Chem. Chem. Phys.* **2020**, *22*, 11644−11651.

(11) Gierke, T. D. Dynamic orientational pair correlations in symmetric tops and static orientational pair correlations in anisometric molecules. *J. Chem. Phys.* **1976**, *65*, 3873−3882.

(12) Braun, D.; Boresch, S.; Steinhauser, O. Transport and dielectric properties of water and the influence of coarse-graining: Comparing BMW, SPC/E, and TIP3P models. *J. Chem. Phys.* **2014**, *140*, 064107.

(13) Keyes, T.; Kivelson, D. Depolarized light scattering: Theory of the sharp and broad Rayleigh lines. *J. Chem. Phys.* **1972**, *56*, 1057−1065.

(14) Kivelson, D.; Madden, P. Theory of dielectric relaxation. *Mol. Phys.* **1975**, *30*, 1749−1780.

(15) Madden, P.; Kivelson, D. A consistent molecular treatment of dielectric phenomena. *Adv. Chem. Phys.* **2007**, *56*, 467−566.

(16) Nadolny, H.; Volmari, A.; Weingärtner, H. Orientational dynamics of hydrogen-bonded liquids—A comparative study of dielectric and nuclear magnetic relaxation in n-butanol-tetrachloromethane mixtures. *Ber. Bunsenges. Phys. Chem.* **1998**, *102*, 866−871.

(17) Volmari, A.; Weingärtner, H. Cross terms and Kirkwood factors in dielectric relaxation of pure liquids. *J. Mol. Liq.* **2002**, *98*, 295−303.

(18) Weingärtner, H.; Nadolny, H.; Oleinikova, A.; Ludwig, R. Collective contributions to the dielectric relaxation of hydrogen-bonded liquids. *J. Chem. Phys.* **2004**, *120*, 11692−11697.

(19) Samanta, T.; Matyushov, D. V. Nonlinear dielectric relaxation of polar liquids. *J. Mol. Liq.* **2022**, *364*, 119935.

(20) Böttcher, C. J. F. Theory of Electric Polarization. *Dielectrics in Time-Dependent Fields*; Elsevier: Amsterdam, Netherlands, 1973; Vol. 2.

(21) Matyushov, D. V. *Manual for Theoretical Chemistry*; World Scientific Publishing Co. Pte. Ltd.: Hackensack, NJ, 2021; DOI: 10.1142/12061.

(22) This definition of the Laplace−Fourier transform defines the signs of the real and imaginary parts in the Cole−Davidson relation and $\tilde{\varepsilon}(\omega)$.

(23) Hansen, J.-P.; McDonald, I. R. *Theory of Simple Liquids*, 4th ed.; Academic Press: Amsterdam, Netherlands, 2013; DOI: 10.1016/C2010-0-66723-X.

(24) Mori, H. Transport, collective motion, and Brownian motion. *Prog. Theor. Phys.* **1965**, *33*, 423−455.

(25) Balucani, U.; Zoppi, M. *Dynamics of the Liquid Phase*; Clarendon Press: Oxford, U.K., 1994.

(26) Harp, G. D.; Berne, B. J. Time-correlation functions, memory functions, and molecular dynamics. *Phys. Rev. A* **1970**, *2*, 975−996.

(27) Wertheim, M. S. Theory of polar fluids—V. Thermodynamics and thermodynamic perturbation theory. *Mol. Phys.* **1979**, *37*, 83−94.

(28) Stell, G.; Patey, G. N.; Høye, J. S. Dielectric constants of fluid models: Statistical mechanical theory and its quantitative implementation. *Adv. Chem. Phys.* **2007**, *48*, 183−328.

(29) Böhmer, T.; Gabriel, J. P.; Zeißler, R.; Richter, T.; Blochowicz, T. Glassy dynamics in polyalcohols: Intermolecular simplicity vs. intramolecular complexity. *Phys. Chem. Chem. Phys.* **2022**, *24*, 18272−18280.

(30) Moch, K.; Münzner, P.; Böhmer, R.; Gainaru, C. Molecular cross-correlations govern structural rearrangements in a nonassociating polar glass former. *Phys. Rev. Lett.* **2022**, *128*, 228001.

(31) Dyre, J. C. Solidity of viscous liquids. III. α relaxation. *Phys. Rev. E* **2005**, *72*, 011501.

https://doi.org/10.1021/acs.jpclett.3c00959
J. Phys. Chem. Lett. 2023, 14, 4886−4891