From Single-Particle to Collective Dynamics in Supercooled Liquids

Dmitry V. Matyushov*,† and Ranko Richert*,‡

†*School of Molecular Sciences and Department of Physics, Arizona State University, PO Box 871504, Tempe, AZ 85287-1504*

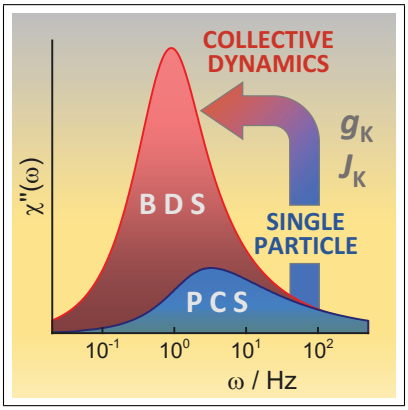
‡*School of Molecular Sciences, Arizona State University, PO Box 871604, Tempe, AZ 85287-1604*

E-mail: dmitrym@asu.edu; Ranko.Richert@asu.edu

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-rank 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. Since 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.

TOC Graphic



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 non-exponential decays correlation of the corresponding time correlation functions associated with structural relaxation, equivalent to asymmetrically broadened susceptibility profiles in the frequency domain.[1] However, the extend 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 temperature, and are material specific even if compared at a common loss peak frequency ($\omega_{\max}$) 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 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 $\omega_{\max}$, the PCS results can be approximated by a Cole-Davidson type function, $\chi''(\omega) \propto \mathrm{Im}\left[(1 - i\omega\tau_{\mathrm{CD}})^{-\gamma}\right]$, 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

$\chi''_{\rm PCS}(\omega)$ and $\varepsilon''_{\rm BDS}(\omega)$ 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 $\lesssim 0.2$).[4]

Based on approximations detailed below, Keyes[9] derived the relation

$$\tau_M = g_{\rm K}\tau_s \tag{1}$$

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 $g_{\rm K}$. Comparing τ_M from BDS with $\tau_s^{(2)}$ from PCS reveals that the ratio $\tau_M/\tau_s^{(2)}$ near T_g exceeds $g_{\rm K}$ by far, assuming values of up to 20 reported for propylene glycol.[10] Moreover, the temperature dependence of τ_M and $\tau_s^{(2)}$ differ by more than can be explained by $g_{\rm K}(T)$ 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] $J_{\rm K}$ resulting in the Keyes-Kivelson-Madden (KKM) relation[9,13–15]

$$\tau_M = (g_{\rm K}/J_{\rm K})\tau_s = (g_{\rm K}/J_{\rm K})\kappa\tau_s^{(2)} \tag{2}$$

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 $J_{\rm K}/\kappa \neq 1$ is essential for translating single-particle into collective loss spectra, i.e., $\chi''_{\rm PCS}(\omega) \rightarrow \varepsilon''_{\rm BDS}(\omega)$, which is the aim of the present work. Calculations based on experimental PCS spectra will then be shown to compare favorably with measured BDS loss profiles. Moreover, experimental evidence shows larger separations between single-particle and collective relaxation times at lower temperatures, consistent with $J_{\rm K}/\kappa$ decreasing with reducing the temperature.

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

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

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 $a = \mathrm{M}, \mathrm{s}$ specifies either the normalized time autocorrelation function of the total dipole moment $\mathbf{M}(t)$ ($a = \mathrm{M}$) or of single-particle dipole orientations ($a = \mathrm{s}$, 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 collective average (integral) relaxation times in eqs 1 and 2

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

with $a = \mathrm{M}, \mathrm{s}$. 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.

In order 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 $\phi_a(t)$, $a = \mathrm{M}, \mathrm{s}$, 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 $\langle \mathbf{M} \cdot \mathbf{M} \rangle = g_{\mathrm{K}} \mu^2 N$ in the denominator in eq 10 is

the product of the squared molecular dipole μ, number of dipoles N in the sample, and the Kirkwood factor

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

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

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

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 Supporting Information (SI) for derivation)

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

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

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

Here, $\langle \dots \rangle^\dagger$ denotes the correlation function propagated in the orthogonal space of Mori's[24] projection operator technique,[23,25] $\langle \dot{\hat{\mathbf{u}}}_1 \cdot \dot{\hat{\mathbf{u}}}_i(t) \rangle^\dagger = \langle \dot{\hat{\mathbf{u}}}_1 \cdot e^{i(1-\hat{P})\mathcal{L}t} \dot{\hat{\mathbf{u}}}_i \rangle$, with $\mathcal{L}$ being the Liouville operator and $\hat{P}$ 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 $\psi_s(0) = \omega_s^2 = 2k_{\mathrm{B}}T/I$ for a symmetric top with the moment of inertia I.

The derivation so 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

$$\tau_{\mathrm{K}} = \tilde{f}_M(0) = \tilde{f}_s(0) \tag{19}$$

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 $\tilde{f}_M(\omega) = J_{\mathrm{K}}\tilde{f}_s(\omega)$. This approximation leads to the following connection between the memory functions

$$\tilde{K}_M(\omega) = (g_{\mathrm{K}}/J_{\mathrm{K}})^{-1}\tilde{K}_s(\omega) \tag{20}$$

To account for the second rank of PCS, we replace the retardation parameter $g_{\mathrm{K}}/J_{\mathrm{K}}$ with ζ_{K} that follows from the second KKM relation in eq 2

$$\zeta_{\mathrm{K}} = (g_{\mathrm{K}}/J_{\mathrm{K}})\kappa \tag{21}$$

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 $\zeta_{\rm K}$

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

We note that simple proportionality between $\tilde{f}_M(\omega)$ and $\tilde{f}_s(\omega)$ cannot be correct in the whole range of frequencies since 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 $\tau_{\rm K}^a$, one would anticipate $\tau_{\rm K}^M=J_{\rm K}\tau_{\rm K}^s=J_{\rm K}\kappa\tau_{\rm K}^{s,(2)}$ and $\tau_{\rm K}^a\omega\ll 1$ in the frequency range applicable to experimental conditions. Both static and dynamic cross-correlations affect t he relation between the single-particle and collective dynamics, but they both can be reduced to numerical scaling factors at su iciently small peak frequencies characteristic of low-temperature (supercooled) liquids.

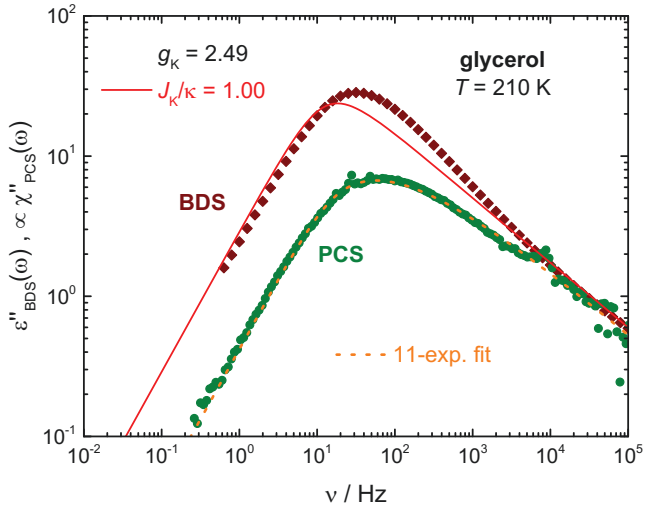


Figure 1: Experimental results for the dielectric loss spectrum $\varepsilon''(\omega)$ (BDS, diamonds) and the photon-correlation susceptibility $\chi''(\omega)$ (PCS, circles) of glycerol at $T=210$ K, taken from Gabriel *et al.*[10] The orange dotted line is a fit to the PCS data, the red solid line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

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, 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

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

Employing 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 SI 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

$$y_{\text{eff}} = (\rho/9\varepsilon_0)\left[(\mu')^2/(k_{\text{B}}T) + 3\alpha'\right] \tag{25}$$

where ε_0 is the vacuum permittivity and ρ is the liquid number density. The polarity

parameter enters the Kirkwood-Onsager equation[28]

$$(\varepsilon_s - 1)(2\varepsilon_s + 1) = 9y_{\text{eff}}\varepsilon_s g_{\text{K}} \tag{26}$$

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 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 the hard-sphere diameter might affect the calculation of g_{K} in Wertheim's formalism (see SI). 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 decreasing temperature. For instance, the value of τ_M/τ_s for propylene glycol increases by 50% when changing 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 $J_{\text{K}} \approx 1$ 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 $J_{\text{K}} = 1$ (eq 1) opposes this assessment. The limit $J_{\text{K}} = 1$ 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 per-

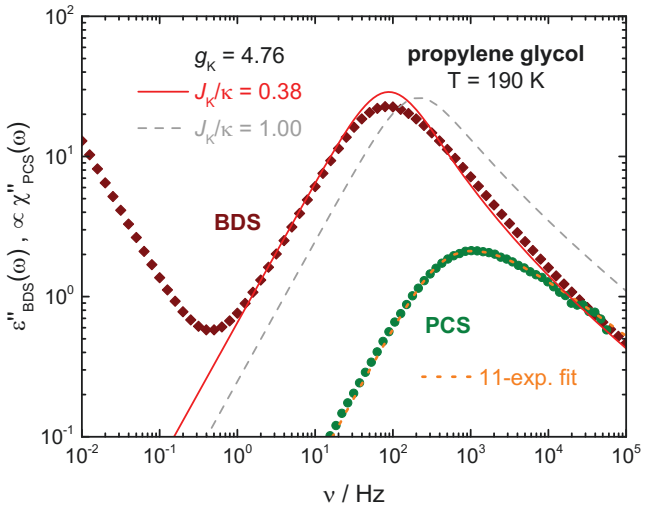


Figure 2: Experimental results for the dielectric loss spectrum $\varepsilon''(\omega)$ (BDS, diamonds) and the photon-correlation susceptibility $\chi''(\omega)$ (PCS, circles) of propylene glycol at $T = 190$ K, taken from Böhmer *et al.*[29] The orange dotted line is a fit to the PCS data, the grey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

formance 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 extensions has allowed us to convert the single-particle correlation function into the collective function by utilizing a single retardation parameter ζ_K (eq 21).

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 SI). [c]Adjusted as a fitting parameter.

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

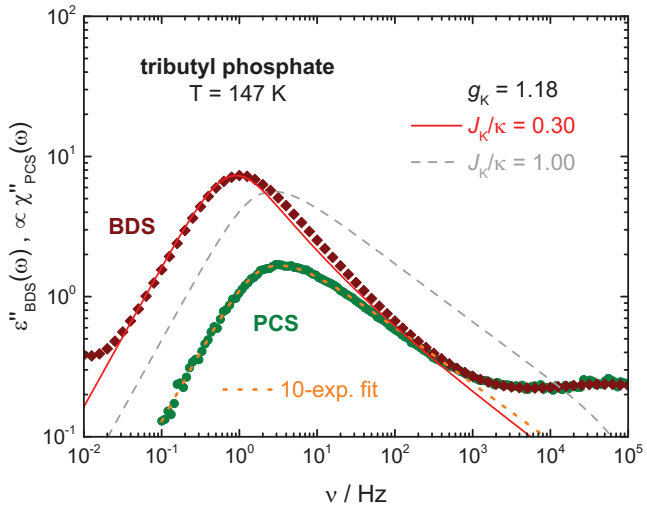


Figure 3: Experimental results for the dielectric loss spectrum $\varepsilon''(\omega)$ (BDS, diamonds) and the photon-correlation susceptibility $\chi''(\omega)$ (PCS, circles) of tributyl phosphate at $T = 147$ K, taken from Pabst *et al.*[7] The orange dotted line is a fit to the PCS data, the grey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

the theory development. This function is directly related to the experimentally observable single-particle response function. One obtains by substituting eq 9 to eq 24

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

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 $P(\omega)$

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

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

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

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 Keyes-Kivelson-Madden 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.

Supporting Information Available

Derivation of the KKM equation and properties of the liquids used in the analysis and calculations of their Kirkwood factors.

Notes

The authors declare no competing financial interests.

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