Stokes-Einstein-Debye Failure in Molecular Orientational Diffusion: Exception or Rule?

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ABSTRACT: The Stokes-Einstein-Debye (SED) expression is used routinely to relate orientational molecular diffusivity quantitatively to viscosity. However it is well known that Einstein's equations are derived from hydrodynamic theory for the diffusion of a Brownian particle in a homogeneous fluid and examples of SED breakdown and failure for *molecular* diffusion are not unusual. Here, using optical Kerr-effect spectroscopy to measure orientational diffusion for solutions of guanidine hydrochloride in water, and mixtures of carbon disulfide with hexadecane, we show that these two contrasting systems each show pronounced exception to the SED relation and ask if it is reasonable to expect molecular diffusion to be a simple function of viscosity.
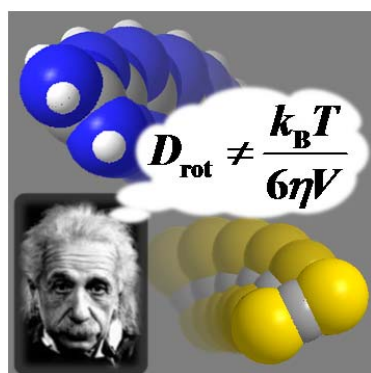
KEYWORDS: Molecular diffusion, diffusivity, relaxation, viscosity, optical Kerr-effect spectroscopy, OKE

That molecular motion is slower in viscous liquids seems self-evident and, perhaps for this reason, despite its simple hydrodynamic basis the Stokes-Einstein-Debye (SED) equation, $D_{\text{rot}} = k_{\text{B}}T/6\eta V$, is used widely to relate the orientational diffusivity D_{rot} of a molecule, through its volume V, to the shear viscosity η of the surrounding liquid. Although often D_{rot} is found to have a linear dependence on η over a limited range of temperature, for small solutes and neat molecular liquids there are observations of SED breakdown and failure.[1-4] Various conditions are invoked to explain these 'exceptions' such as *fractional* SED behavior and *stick* or *slip* regimes. However, for some molecular solutes it has been suggested that specific local interactions are more important than the solvent bulk properties[5,6] and a detailed description of the relation of diffusivity to viscosity may require the solvent structure to be taken into account.[7] Here we investigate two very different systems of mixtures: an aqueous solution of guanidine hydrochloride representing a strongly interacting (hydrogen bonding) liquid, and a mixture of carbon disulfide and hexadecane having only weak (van der Waals) interactions. By varying the composition, we isothermally change the viscosity in each system and observe, in general, no systematic relationship of viscosity to the molecular orientational diffusion.

For the study of molecular dynamics, optical Kerr-effect spectroscopy (OKE) is capable of measuring the low-frequency depolarized Raman spectrum with an unsurpassed dynamic range over the wide spectral range necessary for the accurate determination of intermolecular motions (SI-S1). OKE is sensitive to the orientational motions that change the anisotropic part of the polarizability tensor and therefore the intermolecular spectra of simple liquids can be decomposed into three regions: a prominent band at *ca.* 1-3 THz due to hindered rotations (librations) is connected, by a broad featureless band to the low frequency band that arises from molecular orientational diffusion (*i.e.*, rotational relaxation) (SI-S2).[8,9]

The aqueous solution of guanidine hydrochloride (GuHCl) is much studied[10] due to the outstanding properties of the guanidinium ion (GuH$^+$ = [C(NH$_2$)$_3$]$^+$) as a protein denaturant. GuH$^+$ is highly soluble and relatively 'water neutral', *i.e.*, GuH$^+$:H$_2$O interactions are similar to H$_2$O:H$_2$O interactions. With increasing concentration the viscosity of the solution increases monotonically up to about twice that of neat water for the saturated solution.[11]

GuH$^+$ is planar with high ($D_{3\text{h}}$) symmetry which results in an uncluttered OKE spectrum with a single relaxational mode arising from the out-of-plane orientational diffusion of the ion. Water is relatively invisible to OKE spectroscopy (due to its low, near-isotropic, polarizability), but its rotational relaxation in the solution has been measured by dielectric relaxation spectroscopy (DRS) (for which GuH$^+$, with its zero static dipole moment, is invisible).[11] The chloride ion is isotropic and therefore

makes no direct contribution to rotational relaxation. With its relatively high polarizability, GuH+ then dominates the OKE spectrum of the mixture. Figure 1 shows the spectra for a range of concentrations up to 7.35 M.
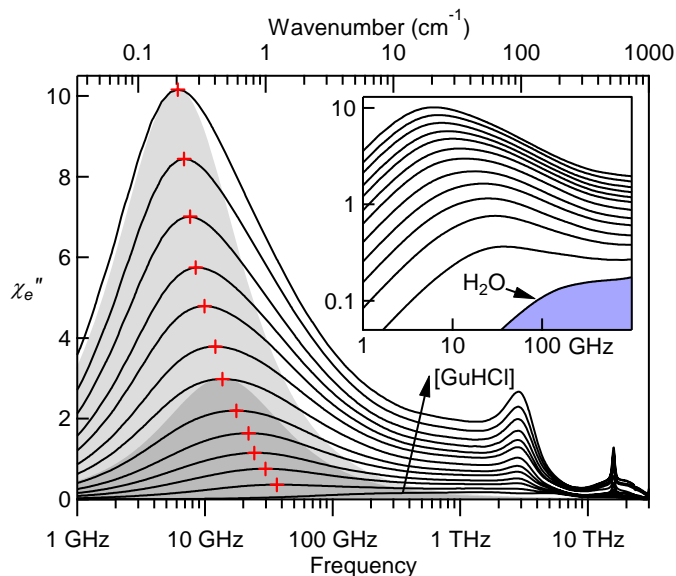
Figure 1 OKE spectra for aqueous guanidine hydrochloride (GuHCl) solution at 25 °C for concentrations from neat water to 7.35 M. The light and dark grey regions are Debye band-shapes revealing the broadening of the (GuH+) relaxation band at lower concentration. Crosses mark the position of the relaxation band maximum. The librational band appears at *ca*. 3 THz. Inset is detail on logarithmic scales showing that the water contribution (blue fill) is minimal at low frequency.

In the solution the rotational relaxation band of GuH+ (at *ca*. 10 GHz ≈ 16 ps) is considerably broader than the simple Debye response. Broadening is often an indication of heterogeneity, so we have to consider the possibility of GuH+ ion clustering or stacking.[11,12] We can show, however, that clustering should cause the heterogeneity to increase with concentration (SI-S3), whereas here the opposite is the case (Figure 1). Leaving aside this complexity, we make the simplest estimate of the rotational relaxation time of the GuH+ ion by taking the reciprocal of the frequency of the relaxational band peak, that is, $\tau_{\mathrm{OKE}} = \omega_{\mathrm{peak}}^{-1}$.

In Figure 2, τ_{OKE} is compared to viscosity along with the rotational relaxation timescale of water measured for the same solution by DRS.[11] It can be seen immediately that in both cases relaxation is decoupled from viscosity. For water, relaxation is effectively independent of concentration, but for the GuH+ ion a linear trend is seen above *ca*. 2 M.

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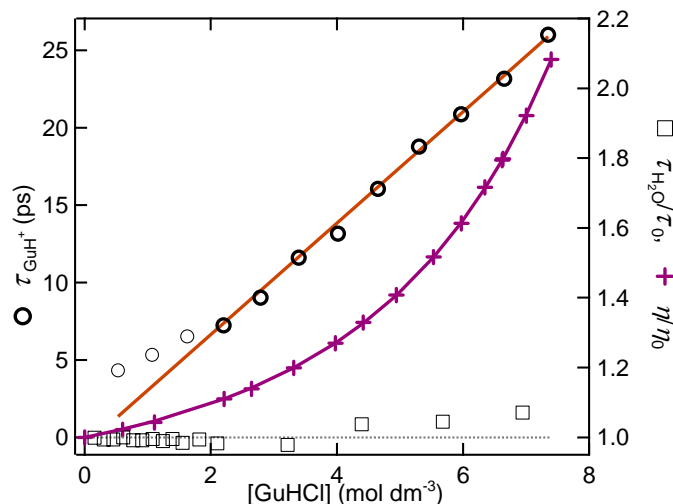
Figure 2 While the viscosity of aqueous GuHCl solution (crosses) increases non-linearly with concentration (up to a factor of >2), the OKE rotational relaxation timescale for the GuH$^+$ ion (τ_{GuH+}, circles) increases linearly above 2 M, and that of the water molecule measured by DRS[11] (squares) barely changes. The viscosity is fit by a Vogel-Fulcher-Tammann type expression.[13]

As strongly hydrogen-bonding systems, exemplified by water and aqueous solutions, are often assumed to be anomalous, we also study the weakly interacting, non-hydrogen-bonding, non-polar system of CS_2 in hexadecane. CS_2 (S=C=S) is a versatile OKE probe having a high polarizability (strong signal) and again high symmetry. It is miscible with the simple hydrocarbon hexadecane ($CH_3(CH_2)_{14}CH_3$) at room temperature over the whole composition range for which the viscosity then varies by almost an order of magnitude (SI-S2). Hexadecane too has a simple spectrum and in the mixture the relaxation timescales of the two components are generally well separated so the effect of concentration on each can be observed.

The OKE spectra for CS_2:hexadecane are shown in Figure 3. In neat CS_2 the rotational relaxation (at ~90 GHz ≈ 1.8 ps) overlaps the librational mode (at ~1 THz) but at low temperature can be resolved as a Debye lineshape (Figure 3(a)). The hexadecane mixtures, however, cannot be cooled far without crystallization so measurements were made at 20 °C. Hexadecane has a relatively weak spectrum of typical characteristic form with a broad librational band at *ca.* 1 THz and a very dominant rotational relaxation peak at *ca.* 400 MHz. This mode has a Debye lineshape (*i.e.*, a simple exponential decay in time) with, in the neat liquid, a time constant of 392 ps.
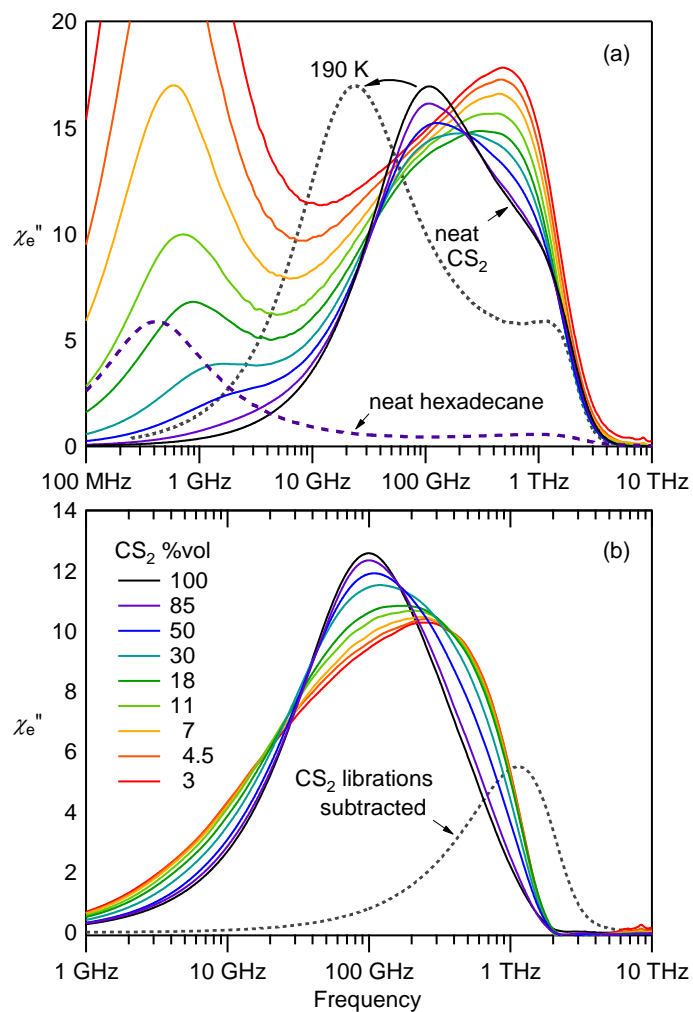
Figure 3 (a) OKE spectra at 20 °C for the CS_2:hexadecane mixture ranging from 3% (red) to 100% volume ratio (black) of CS_2. The spectra are normalized to the area of the CS_2 bend (at 19.6 THz) so that changes in the CS_2 contribution can be seen. The neat hexadecane spectrum at 20 °C, arbitrarily scaled, is also shown (dashed). On cooling CS_2 (dotted), relaxation slows. This is the behavior that would be expected if SED applied and the relaxation slowed by a factor consistent with the (9x higher) viscosity of the 3% CS_2 solution. **(b)** After subtraction of both the hexadecane contribution and the CS_2 librational contribution (dotted) it is clear that the CS_2 relaxation timescale does not follow the large change in viscosity; rather there is an overall shift to higher frequency, *i.e.,* an inverse correlation. The mode also becomes increasingly broadened as CS_2 concentration falls (not simply due to the heterogeneous environment of the mixture as the broadening continues to increase down to 3% CS_2 concentration).

To resolve the CS_2 relaxation contribution the hexadecane contribution was fitted and then subtracted along with the CS_2 librational band (SI-S2). The resultant spectra, principally the CS_2 relaxation, are shown in Figure 3(b). On increasing hexadecane concentration the CS_2 relaxation mode broadens but, despite the large increase in viscosity, there is no evidence of a simple shift of the

relaxation to lower frequency. Instead the first moment of these spectra shows (Figure 4) an inverse correlation of timescale with viscosity until above *ca.* 80% hexadecane concentration ($\eta \approx 1.7$ cP) where the change becomes mostly broadening. In a fashion reminiscent of the guanidinium solution, the broadening is greatest when the mixture is almost 100% hexadecane.
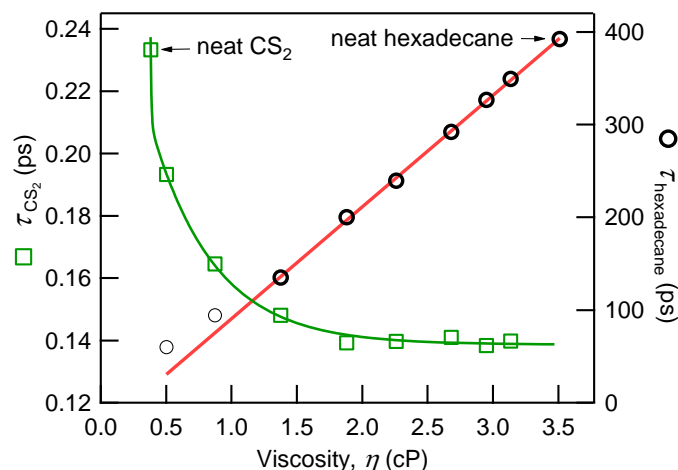
Figure 4 CS_2 time constant (reciprocal of 2π × 1st moment of the relaxation band in Figure 3(b)) (squares) and Debye time constant for hexadecane relaxation (circles) *vs.* viscosity for CS_2:hexadecane mixtures showing a linear correlation (SED behavior) (except at very low hexadecane concentration) for hexadecane relaxation and an anti-correlation for CS_2 relaxation. The seven highest data for hexadecane are fit by the line 120.5 (±1.3) × η -30 (±3).

Despite this surprising behavior the hexadecane relaxation timescale does increase with increasing hexadecane concentration. In Figure 4 the Debye time constant τ is also plotted against viscosity and, for the first time, we see a linear dependence, in agreement with SED, except at the lowest hexadecane concentrations (low viscosity) where the measurement becomes unreliable as the hexadecane relaxation band merges with that of CS_2.

As the SED equation relates viscosity to molecular diffusivity through the *effective* molecular volume V_{eff}, the latter can be calculated from the gradient of the plot of τ *vs.* viscosity (provided there is a linear relationship). For pure rotations, the rate of the decay due to the second rank polarizability tensor (applicable to OKE studies) is proportional to $6D_{rot}$. Hence the molecular rotational relaxation Debye time-constant (proportional to $1/6D_{rot}$) is given by $\tau_{rot} = V_{eff}\eta / k_B T + \tau_{rot}^0$. The fit in Figure 4 for hexadecane yields a gradient of 120.5 (±1.3) ps cP^{-1}, hence, $V_{eff} = 120.5 k_B T$ ps cP$^{-1} = 488 \pm 5 \text{Å}^3$.

For comparison, the effective molecular volume of hexadecane in the neat liquid implied by the room-temperature density of 0.77 g cm^{-3} and relative molar mass of 226.44 is 488 Å^3. Given the crudeness of this calculation—with no corrections for aspect ratio or boundary conditions—there is

clearly some fortune involved in the agreement, but it appears that in this system hexadecane behaves as SED predicts.

In contrast to the simple first order dependence of diffusivity on viscosity that would be predicted if SED held, the behavior of each component of these two binary mixtures ranges from the complete decoupling exhibited by water in GuHCl solution to the *counter*-SED behavior of CS_2 and ideal SED behavior of hexadecane in CS_2:hexadecane mixtures.

Although it has been proposed that the temperature dependence of orientational relaxation in neat water follows the SED relation,[14] it is now generally accepted that the OKE relaxation signal for water has a complex non-exponential decay arising primarily from translation motion (SI-S3). It is also known that water has an expanded structure in which the hydrogen-bonded molecules reorient through a complex large-angle 'jump' process, which, although an activated process, is not diffusional,[15] and the rate of relaxation is primarily determined by the rate of hydrogen bond fluctuations. Furthermore, in simple salt solutions the orientational relaxation of the water molecule, as a function of concentration, is generally uncorrelated with viscosity.[6,11,13] Here, the presence of a high concentration of the large GuH^+ ions does not strongly influence the relaxational rate, hence it appears that H_2O forms hydrogen bonds to both GuH^+ (and chloride ions) that are of similar strength to H_2O-H_2O hydrogen bonds. We can say that water is an extreme case of a molecular liquid, characterized by strong directional bonding.

In contrast, the relaxation timescale of the GuH^+ ion has an apparently linear dependence on concentration but this is markedly different to the nonlinear viscosity increase. This linear trend, which breaks at *ca*. 2.1 M, suggests a simple dependence on concentration rather than viscosity. At the highest concentration of 7.35 M, each GuH^+ ion has $(6.1 \text{ Å})^3$ of space in which there are only 3.5 H_2O molecules and 1 chloride ion. At the lowest concentration of 0.53 M, each GuH^+ ion has $(15 \text{ Å})^3$ of space in which there are *ca*. 100 H_2O molecules. Therefore at low concentration the GuH^+ ion is effectively surrounded by bulk water (and its dynamics are determined by collisions with water molecules that are relatively mobile (but not by the bulk viscosity). The break in the line at 2.1 M suggests a transition to the regime where GuH^+:GuH^+ collisions become the dominant factor in the orientational diffusion rate.

As both CS_2 and hexadecane are non-polar non-hydrogen bonding molecules, in their mixture the principal attractions are van der Waal forces. Nevertheless, the relaxation of CS_2 is still clearly decoupled from viscosity. As hexadecane is added to CS_2, the CS_2 relaxation appears to speed up even as the viscosity is increasing. Although this measurement is partially obscured by the broadening of the

band, there is emphatically no evidence of the substantially slower relaxation that would be expected from SED behavior.

The broadening of the CS_2 relaxation band could arise from heterogeneity reflecting the different environments although the broadening is still increasing at the lowest (3%) volume ratio where it would be expected that each CS_2 molecule is completely surrounded by the alkane. This perhaps suggests that the alkane itself presents a heterogeneous environment to CS_2 perhaps due to variations in the packing or ordering of the hydrocarbon chains.

The exception then is hexadecane that behaves in the mixture with CS_2 (over most of the compositional range) as an ideal SED probe. As hexadecane interacts only weakly, the high viscosity of neat hexadecane must result from steric interactions combined with its relatively large bulk and high aspect ratio. The viscosity falls rapidly at low CS_2 concentration as the chains are diluted by the more mobile molecule.

The Stokes-Einstein-Debye relation has been applied widely to molecular orientational diffusion on both a qualitative and quantitative basis,[16-22] but whereas for large probe particles, such as colloids and fluorescent tracers, there is often excellent agreement, in general, for molecular diffusion poor agreement is found. Corrections are then made: for example to account for molecular shape and boundary conditions (such as dielectric friction effects and *stick* or *slip* surface interactions).[3,4,23] Deviations from SED are read as evidence of structural changes,[24-26] and often *fractional* forms of the Stokes-Einstein (for translational diffusion) and Stokes-Einstein-Debye relations are interpreted as evidence of a change in effective volume with temperature[2,27-29] for example due to cooperative rearrangement in supercooled liquids.[30]

But, since SED is based on hydrodynamics, and applies strictly to a particle immersed in a homogeneous fluid, there is little reason (as Einstein made clear in his 1906 paper[31]) to expect it to apply on a molecular scale. Here, for these two contrasting systems, it is clear that SED does not generally apply. This suggests that diffusion of molecular-size particles is dominated by local interactions that decouple the diffusivity from the bulk viscosity. This would be consistent with the observation of the anomalous speeding up of CS_2 relaxation in the hexadecane mixture reflecting that the CS_2–hexadecane interactions are weaker than the CS_2–CS_2 interactions. A molecule is apparently aware of only short range interactions, primarily then to its first solvation shell, and application of the Stokes-Einstein and Stokes-Einstein-Debye relations in studies of molecular self-diffusion must be made cautiously. It has indeed been suggested before that a critical particle volume exists below which the SE relation (for translational diffusion) fails, and molecular dynamics (MD) simulations for a

Lennard-Jones liquid[32] suggest a critical volume, in the nanometre range, below which local intermolecular forces dominate the translational mobility.

The exception here is hexadecane in CS_2 mixture, which appears to obey SED remarkably well. As hexadecane is still relatively small, this suggests that the nature of the intermolecular forces, which in this case are weak and diffuse, is as important as the molecular size. Therefore, calculations of a critical size for SED behavior are unlikely to hold over a wide range of liquids.

Taken together, this evidence suggests that molecular orientational diffusion is controlled by local (first solvation shell) interactions rather than by the bulk properties of the liquid. These simple observations raise, of course, the question of the true relationship of diffusion to viscosity. But, because of this complexity and the distinct relaxation mechanisms that contribute,[33,34] only detailed MD calculations are likely to be able to predict such a relationship,[7] and there is no simple theory that is able to predict the value of viscosity from molecular properties.

The observations suggest that in the case that a molecule can support numerous weak interactions (hexadecane) the single molecule motion could correctly be termed diffusive, and SED is then obeyed, whereas if the interactions are dominated by a small number of strong interactions, then orientational relaxation is not diffusive, and SED is not obeyed. We suggest that the majority of liquids composed of small molecules fall into the second category. Since SED is widely used a method of identifying anomalous behavior in molecular liquids, it is essential that such distinction can be made and this calls for a systematic approach to predict, perhaps through MD simulation, the nature of single molecule relaxation.

Often, temperature dependent measurements do show similar trends in viscosity and molecular diffusion (and in these cases the SED relation will remain an important metric), but as both processes are activated this is unsurprising and is not evidence of a causal relationship. Hence, whilst there are systems for which the application of SED is appropriate (*e.g.*, nanometre-scale probe molecules used for studies in homogeneous solvents), the apparent observance of SED in other liquids should be treated with caution.

Supporting Information Available: (S1) Experimental details: optical Kerr-effect measurements, sample preparations. (S2) optical Kerr effect principles, time-domain data, details of fitting and analysis,

viscosity measurements. (S3) Calculation of the effect of clustering on OKE spectra. This material is available free of charge at http://pubs.acs.org.

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Supporting Information

S1. Methods

The OKE data were recorded in the standard time-domain step-scan pump-probe configuration. A laser oscillator (Coherent Micra) provided ~10 nJ pulses with a nominal wavelength of 800 nm at a repetition rate of 82 MHz. After pre-compensation for group-velocity dispersion in a *Homosil* prism pair, the beam was split into (90%) pump and (10%) probe beams. A high speed optical delay line (Newport IMS600LM) in the pump beam path controlled the pump-probe relative delay with sub-fs resolution. The two beams were then co-focused by a 10 cm focal length achromatic lens into the sample. The transmitted probe beam was recollimated by a matching lens and then analyzed by the combination of an achromatic quarter-wave retarder, Wollaston prism, and balanced photodiode detector. This combination measures the ellipticity of the polarization of the beam induced by the transient birefringence of the sample (optical-heterodyne detection) and hence linearizes the dependence of the measurement on laser power. The optical material in each beam was equalized in order to match the optical dispersion and the cross-correlation measured in the sample implied a pulse duration of typically ~20 fs. To minimize spurious signals from scattered pump light, both pump and probe beams were mechanically chopped at rates of ~3 kHz in the ratio of 5:7 with lock-in demodulation at the difference frequency.

For the longer-timescale relaxation measurements a second set of data was taken in a similar configuration using a higher pulse energy of typically 1 μJ (depending on the sample) provided by a regeneratively-amplified laser (Coherent Legend Elite USX) at a repetition rate of 1 kHz with a pulse duration stretched to ~1 ps. Stretching the pulse enables a higher energy to be used without sample damage or nonlinear effects, and reduces the upper bandwidth limit allowing large step size scanning without introducing undersampling artifacts.

Guanidinium chloride (>99.9%), carbon disulfide (>99.9%), hexadecane (99.9%) and water (>99.9%) (all Sigma-Aldrich), were used as supplied. The guanidine hydrochloride solutions were prepared by weight and converted to molarity via the densities measured by Kawahara et al. [1]. The CS_2 hexadecane solutions were made up as volume ratios. All the liquids were degassed at some point in the preparation.

Before measurement, the samples were centrifuged, to remove particles, and placed into 2 mm pathlength quartz cuvettes. The temperature of the samples was controlled by enclosing the cuvette in a copper block attached to a thermoelectric (Peltier) device controlled by a Melcor MTTC-1410 calibrated to <0.25 K.

S2. Supplementary figures and theory

OKE principles

Optical-Kerr Effect spectroscopy measures the equivalent of the Bose-Einstein-corrected depolarized Raman spectrum in the time domain. That is the derivative over time of the two-point time-correlation function of the anisotropic part of the many-body polarizability tensor **Π,**

$$\chi(t) \propto d/dt \left\langle \mathbf{\Pi}_{xy}(t)\mathbf{\Pi}_{xy}(0) \right\rangle. \qquad (1)$$

The technique is hence sensitive to changes in the anisotropic part of the polarizability tensor and therefore principally to rotational fluctuations. A Fourier-transform deconvolution yields the spectrum corrected for the finite duration of the laser pulse. Yielding excellent sensitivity up to typically tens of terahertz, OKE is a powerful probe of the intermolecular region of liquids.

For the high symmetry ($D_{\infty h}$) CS_2 molecule, orientational relaxation according to Debye's small-step diffusion model is expected to generate a simple exponential decay [2] or, in the frequency domain, the Debye function $D(\omega) = (1 + i\omega\tau)^{-1}$. This decay was observed from the earliest studies of simple liquids, but, in addition, a second fast process was observed that the contemporary theories did not predict [3]. This mode was assigned to the (ensemble) orientational vibration of the molecule in the intermolecular potential well [4-6]. The damped nature of this mode was explained by dephasing due to the inhomogeneity of the liquid structure arising from local density fluctuations. This 'libration' had been identified for some time in dielectric studies [7,8] and has since been studied through theory and simulation [9-11]. These two processes, α relaxation and libration, constitute the simple bimodal model of intermolecular dynamics, but real spectra are inevitably more complex (Figure 1.).
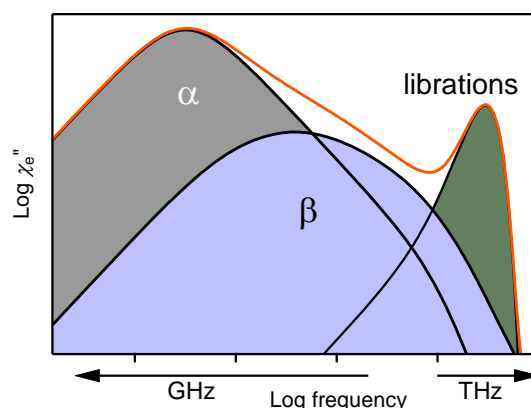

Figure 1.   Model of the intermolecular (OKE) spectrum (imaginary part) for a simple liquid. At the lowest frequency is the single-molecule orientational diffusion (α relaxation). At *ca*. 1–3 THz is the librational band. These two distinct modes are connected by an intermediate process, labeled here as the β relaxation.

In OKE and dielectric studies it is often stated that at the lowest frequencies the fundamental structural relaxation is probed (often without a clear understanding of what this property is). The observations of well-resolved relaxational processes in the two liquid mixtures measured here make it clear that OKE spectroscopy is sensitive simply to (the ensemble average of) the rotational relaxation of the individual components of the liquid. The agreement between the neat liquid spectra and those of the mixtures shows that the signal is simply the sum of the individual contributions; there is no evidence here of collective relaxation processes.
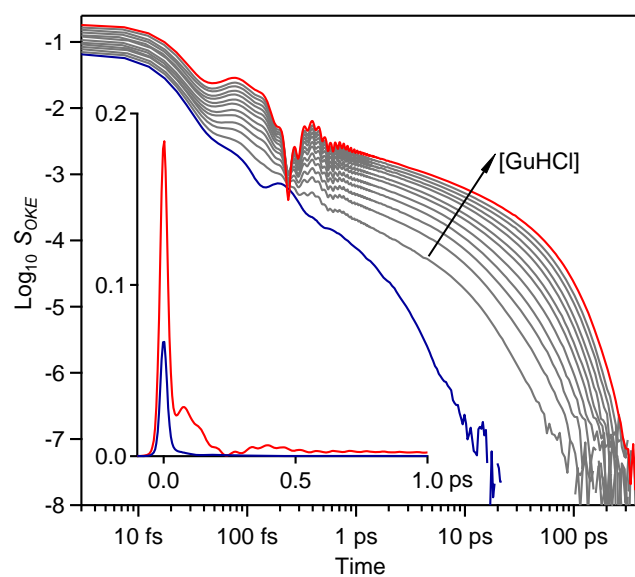
Time domain OKE data

Figure 2.   Logarithmic plot of the raw time-domain OKE data for neat water (blue) and the GuHCl solutions for the concentrations: 0.53, 1.07, 1.63, 2.20, 2.79, 3.39, 4.01, 4.65, 5.30, 5.97, 6.65, 7.35 mol dm^{-3}. The data for the highest concentration are shown in red for clarity. The 'fast' and 'slow' measurements are matched over an order of magnitude in time then spliced at *ca*. 1.5 ps. Inset is detail on linear scales.
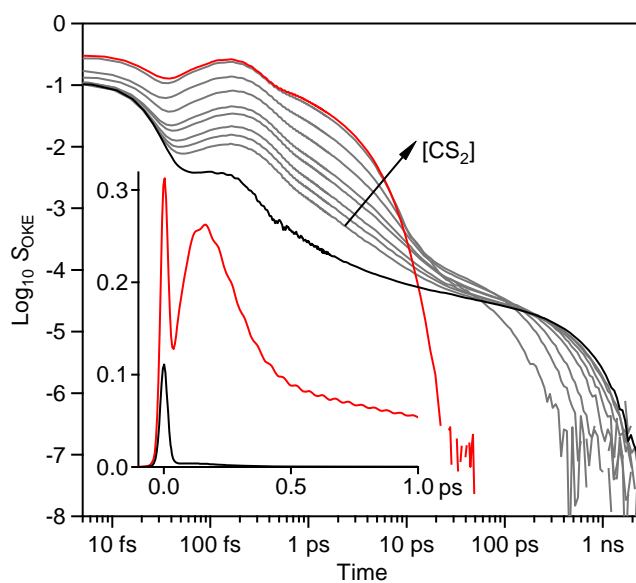

Figure 3.   Raw time-domain OKE data for the CS_2:hexadecane mixtures, from neat hexadecane (black), the mixtures: 0.03, 0.045, 0.07, 0.11, 0.18, 0.30, 0.50, 0.85 volume fraction CS_2 and neat CS_2 (red).
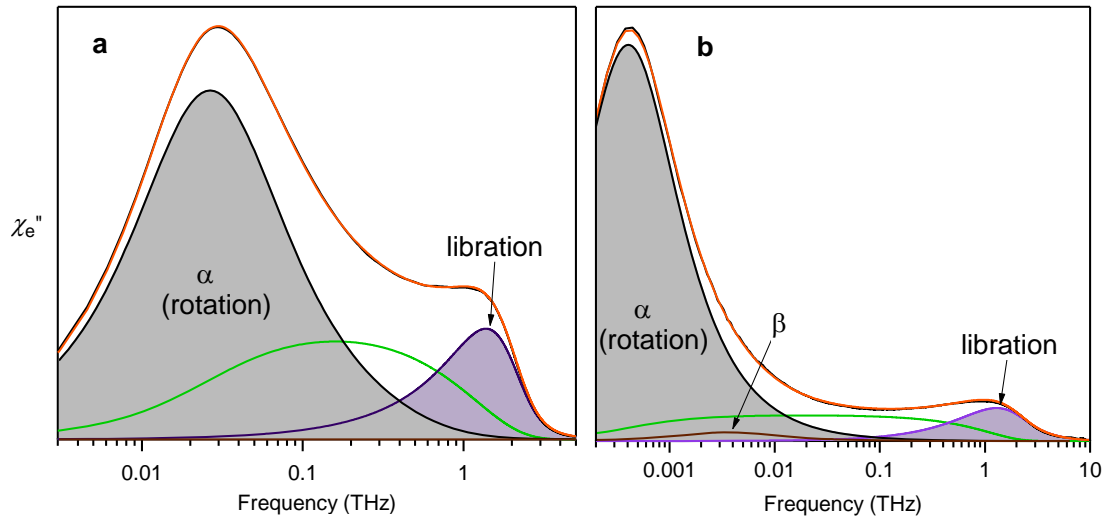
The OKE spectrum for neat CS₂ and hexadecane

Figure 4. Fit of the OKE spectra (black) for (**a**) neat CS₂ at 200 K and (**b**) neat hexadecane at room temperature. The fit (orange) is decomposed into the α relaxation (grey fill), (modified) logarithmic decay (green) and librations (purple). For hexadecane an additional weak β relaxation is observable. Each spectrum is scaled to the peak maximum. The fit parameters are in Table 1.

The OKE spectra for both CS₂ and hexadecane have a relatively simple appearance. In each case the librational band peaks at *ca*. 1.5 THz with a pronounced relaxation peak at 27 GHz in CS₂ and 400MHz in hexadecane. Both α relaxations can be fitted by a Debye function (with an additional weak relaxation in hexadecane perhaps due to nominal axial rotation). This simple relaxation suggests that the conformation of the hydrocarbon does not vary widely on timescales greater than the relaxation timescale. The broad region connecting the relaxation and librations is fit by a logarithmic decay (t^{-1}, in the time domain, or *constant loss* in the frequency domain). Such responses have been identified previously in polymeric and supercooled liquids [12-14] and ionic liquids [15]. To be physical, the logarithmic decay is here modified by the inertial rise function and α relaxation termination. The librational band is a Gaussian-Brownian convolution [5,16]. Further details can be found in [15].

The fit parameters are shown in Table 1. In addition, the modified logarithmic decay is the Fourier transform of

$$S(t) = A\left(1 - \exp\left[-\Gamma^2 t^2\right]\right) t^{-1} \exp\left(-t/\tau\right), \tag{2}$$

where the amplitude $A = 0.0022$, the inertial rise rate Γ was fixed at 5 THz, and τ is the time constant of the α relaxation. The librational mode is reproduced by the Gaussian-Brownian convolution given by the Fourier transform of

$$S(t) = A \exp\left[-\frac{\beta t + \gamma^2 t^2}{2}\right] \frac{\text{Sin}\left(t\sqrt{\omega_0^2 - \beta^2/4}\right)}{\sqrt{\omega_0^2 - \beta^2/4}}, \tag{3}$$

where β is the Brownian damping factor and γ is the Gaussian width factor.

Table 1. Fit parameters for $C_{16}H_{34}$ and CS_2 (Figure 4.). The low value of ω_0 for $C_{16}H_{34}$:GB indicates extreme overdamping.

	$C_{16}H_{34}$				CS_2 200 K			
mode	A /a. u.	τ /ps			A /a. u.	τ /ps		
α	1.1	392			0.72	5.97		
β	0.023	44			-	-		
	A /a. u.	γ /THz	β /THz	ω_0 /THz	A /a. u.	γ /THz	β /THz	ω_0 /THz
GB	1.13	1.02	4.5	0.0065	10.5	0.50	1.1	1.46

The rotational time constant for CS_2

To extract the relaxational time constant for CS_2 both the hexadecane spectrum and the CS_2 librational contribution were subtracted from the spectra of the mixtures. It is impractical to fit the hexadecane contribution in the mixture spectra due to the much stronger CS_2 contribution so these spectra were estimated using the fit function in Figure 4. To do this the Debye contribution was fitted and the remaining bands were fixed except for the amplitudes, which were scaled to the Debye intensity. This may be inaccurate due to changes to the librational linewidth and frequency, but these discrepancies are likely to be small and as this spectrum is weaker than that of CS_2, especially at higher CS_2 concentration, the results appear satisfactory. The librational contribution for CS_2 was then subtracted as a band of fixed lineshape, determined by fitting the neat CS_2 spectrum, that was scaled to produce a flat baseline above 2 THz on subtraction.

Viscosity of the CS_2 hexadecane mixture

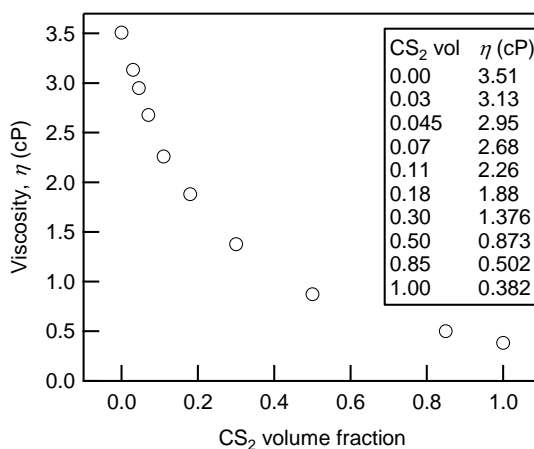The viscosity was measured using a Cambridge Viscosity ViscoLab 3000 at 20 °C.

CS_2 vol	η (cP)
0.00	3.51
0.03	3.13
0.045	2.95
0.07	2.68
0.11	2.26
0.18	1.88
0.30	1.376
0.50	0.873
0.85	0.502
1.00	0.382

Figure 5. Measured viscosity of the CS_2:hexadecane mixture

SED analyses

The data in the main paper for GuHCl are presented as a function of concentration, to facilitate comparison with other studies of salt solutions, whereas the data for the CS_2:hexadecane mixtures are shown on a SED plot with time constant as a function of viscosity. For completion, Figure 6. shows all this data as a function of mol. fraction. The linear dependence of viscosity on CS_2 mol. fraction is clearly seen.
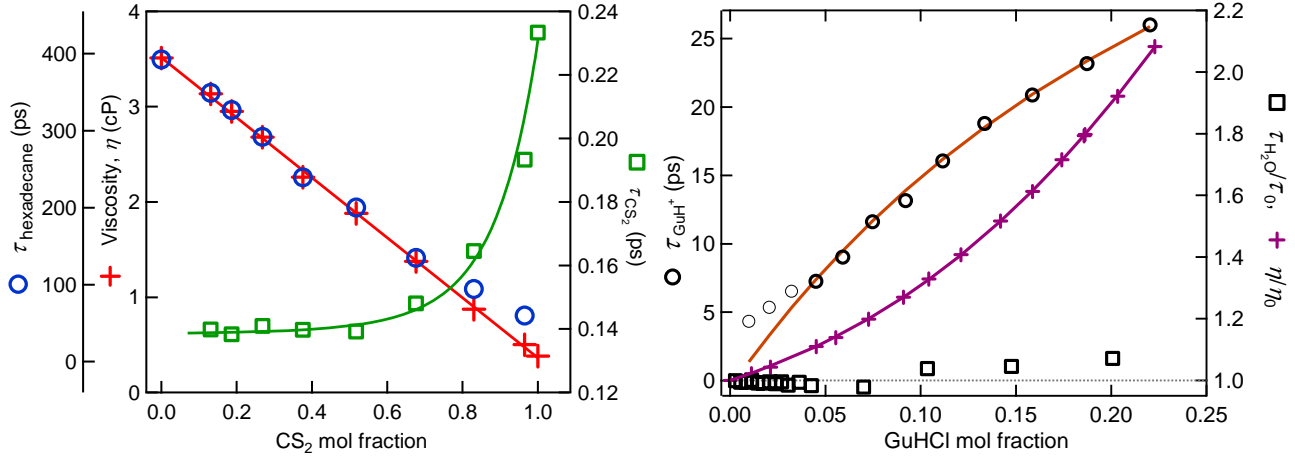

Figure 6.   Comparison of data on a mole fraction scale for (left) CS_2:hexadecane, and (right) aqueous GuHCl solution. The red line is a fit to the viscosity for CS_2:hexadecane showing a simple linear dependence. Other details as the main paper.

S3. Supplementary Notes

OKE relaxation in neat water

Early studies of water interpreted the weak relaxation signal as an exponential or multi-exponential decay but with no consistency between the measured time constants. Righini and co-workers then established that the decay, over the temperature range of 254 K – 314 K, was non-exponential and could be fitted by (the derivative of) a stretched exponential.[17] In their mode-coupling theory (MCT) analysis they fitted the resultant time constant by a power law $\tau(T) \propto \left(T - T_S\right)^{-\gamma}$, where T_S corresponds to the MCT singular temperature. The parameters obtained were T_S = 221 ± 5 K and γ = −2.2 ± 0.3. Fitting viscosity data for water[18] (273 K – 314 K) by the same expression yields T_S = 226 ± 0.06 K and γ = −1.64 ± 0.002. The difference in exponent implies a "fractional SE/SED" relationship.

In the main paper we discuss the relaxation timescale measured by dielectric relaxation for water in the GuH^+ solution as this clearly measures the orientational relaxation (of the strong dipole moment). In comparison, as water has a very weak anisotropy of polarizability,[19] the orientational OKE signal is very weak and it is likely that the decay predominantly comprises (interaction-induced) translational contributions.

The effect of clustering on terahertz spectra

The probability a solute clustering in solution can be calculated as a probability distribution function if a reasonable estimate can be made of the free energy as a function of cluster size.

In Gibbs classical nucleation theory [20,21] the change in free energy of a nucleating cluster of radius r is the sum of a term proportional to the surface area and a term proportional to the volume,

$$\Delta G\left(r\right) = \frac{4}{3}\pi r^3 \Delta G_b + 4\pi r^2 \gamma_{sl}, \tag{4}$$

$$S\left(t\right) = A\left(1 - \exp\left[-\Gamma^2 t^2\right]\right)t^{-1}\exp\left(-t/\tau\right), \tag{5}$$

where ΔG_b is the change of free energy per unit volume of the cluster and γ_{sl} the interfacial energy (or surface free energy or interfacial tension) [20]. ΔG_b can be written in terms of the concentration C of the solute as

$$\Delta G_b = -\frac{k_B T}{\Omega} \ln\left(\frac{C}{C_0}\right), \tag{6}$$

where C_0 is the equilibrium concentration or solubility, and Ω the volume of the cluster. Thus, when the concentration is equal to the equilibrium concentration, $\Delta G_b = 0$, whereas in a supersaturated solution ($C > C_0$), ΔG_b is negative favoring nucleation. Thus, the change in free energy is

$$\Delta G(r) = -\frac{4}{3}\frac{k_B T}{\Omega}\pi r^3 \ln\left(\frac{C}{C_0}\right) + 4\pi r^2 \gamma_{sl}. \tag{7}$$

In non-supersaturated solutions, the probability of finding a cluster of a particular size is

$$P(r) \propto \exp\left(-\Delta G(r)/k_B T\right). \tag{8}$$

The probability distribution for a cluster of n molecules, where $n\Omega = 4/3\pi r^3$ is then

$$P(n) \propto \left(\frac{C}{C_0}\right)^n \exp\left(-\frac{g}{k_B T}n^{2/3}\right), \tag{9}$$

where $g = 6^{2/3}\pi^{1/3}\Omega^{2/3}\gamma_{sl}$.

Figure 7. shows the distribution function Eq. (9)for low concentration, medium concentration, and saturation for $g/k_B T = 1$. Of course, Eq. (9) diverges at large n for $C/C_0 > 1$ because unlimited growth to the crystalline state is favored.
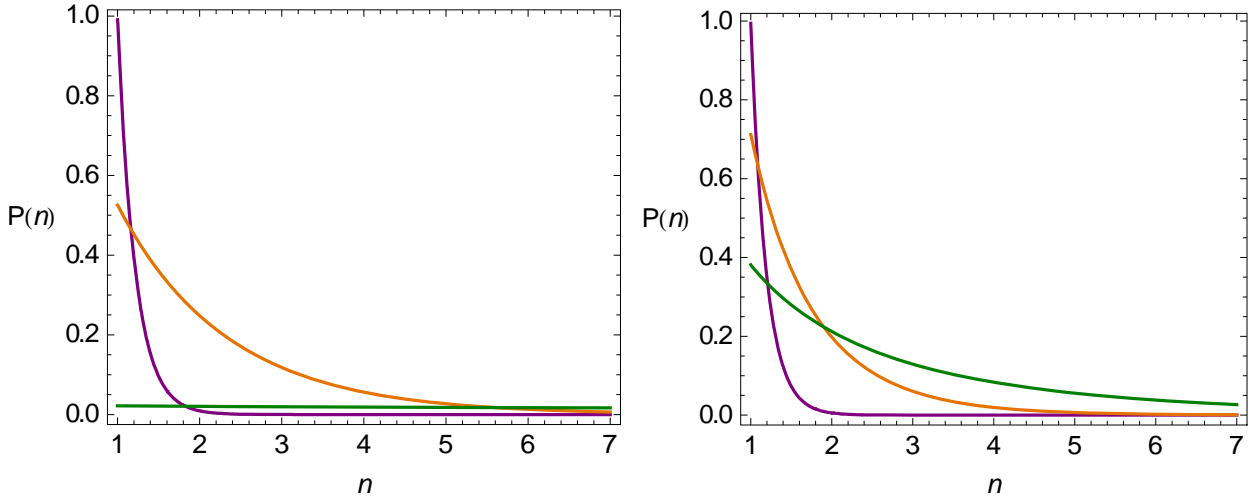

Figure 7. Probability to find a cluster of n molecules for C/C_O = 0.01, 0.5, and 1 (purple, orange, green) for $g/k_B T$ =0. 1 (left) and $g/k_B T$ =1 (right).

Table 2 gives some typical interfacial energies. For guanidinium, estimated values of γ = 1 mJ m^{-2} and Ω = (6×6×2) Å^3 gives $g/(k_B\ 295\ \text{K})$ = 0.2. The probability distribution functions calculated here are similar to the stacking distributions found in molecular dynamics simulations of aqueous guanidinium chloride solution [22]. Thus, for non-supersaturated solutions, the probability of finding clusters is a decaying function of cluster size given by Eq. (9) with $g/k_B T \approx 0.1$ to 1.

Table 2. Interfacial energies γ for four different solutions [23-26]

Solute	Solvent	γ /mJ m^{-2}
maltitol	water	7.4
calcium sulfate dihydrate	isopropyl alcohol	5.6
urea	methanol	1.3
acetic acid	(neat)	15.5

In optical Kerr effect spectroscopy and dielectric relaxation spectroscopy [27-30], simple orientational relaxation is observed as a band described by the Debye function

$$\chi(\omega) \propto \frac{1}{1+i\omega\tau},\qquad(10)$$

where τ, the orientational relaxation time, is proportional to the reciprocal of the single-molecule diffusivity. This is a function of the moment of inertia I and in the simplest cases $D \propto 1/\sqrt{I}$. For the crude approximation that the cluster is a sphere, $I \propto Mr^2$, where M is the mass, and r the radius, hence $I \propto n^{5/3}$ and $\tau \propto n^{5/6}$. Thus, for a distribution of cluster sizes, one would expect a spectrum of the form

$$\chi(\omega) \propto \sum_n \frac{P(n)}{1+i\omega n^{5/6}\tau_0}.\qquad(11)$$

This spectrum is broadened with respect to a standard Debye function and the degree of broadening increases as the cluster size distribution broadens (*i.e.*, as the concentration C approaches the saturation concentration C_0), Figure 8.
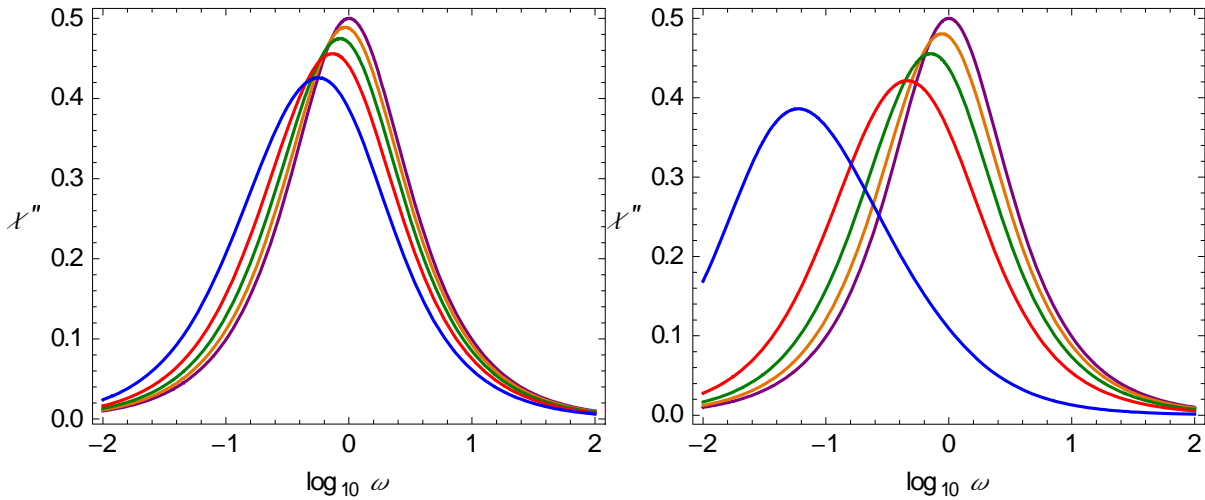

Figure 8. Dielectric or OKE response for a cluster distribution according to Eq. (11) for $C/C_0 = 0$ (purple), 0.25, 0.5, 0.75, and 1 (blue) for $g/k_BT = 1$ (left) and $g/k_BT = 0.1$ (right).

Thus, the same procedure is applied as in the main paper: the effective relaxation time τ' is defined as the angular frequency where the spectral function peaks ($\tau' = 1/\omega_{\mathrm{peak}}$). These concentration-dependent effective relaxation times are plotted in Figure 9. for a number of values of g/k_BT. In all cases, the relaxation time has a strongly nonlinear dependence on concentration. Therefore, with this and the observed *decrease* in linewidth with concentration, it can be concluded that clustering of the guanidinium ions is inconsistent with the observations in the main paper.
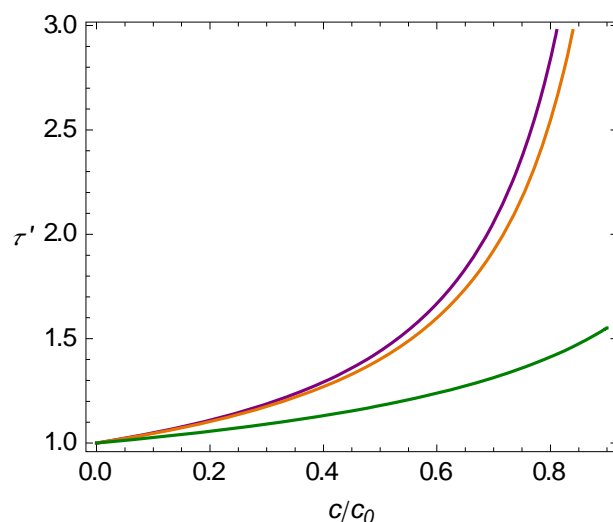
Figure 9. Relaxation timescale, corresponding to the maximum in the dielectric or OKE response, for a cluster distribution according to Eq. (11) for $g/k_B T$ = 0.01 (purple), 0.1 (orange) and 1 (green).

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