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

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S *Supporting Information*

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.
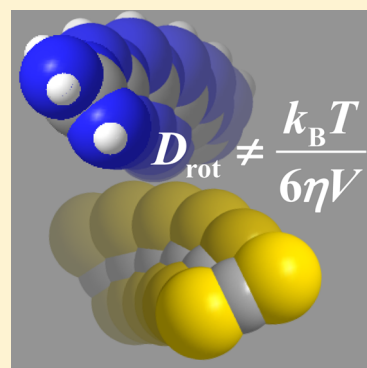
$$D_{rot} \neq \frac{k_B T}{6 \eta V}$$

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, $D_{rot} = k_B T / 6 \eta V$, 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 (section S1, Supporting Information). 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) (section S2, Supporting Information).[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_2O interactions are similar to H_2O:H_2O 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_{3h}) 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.
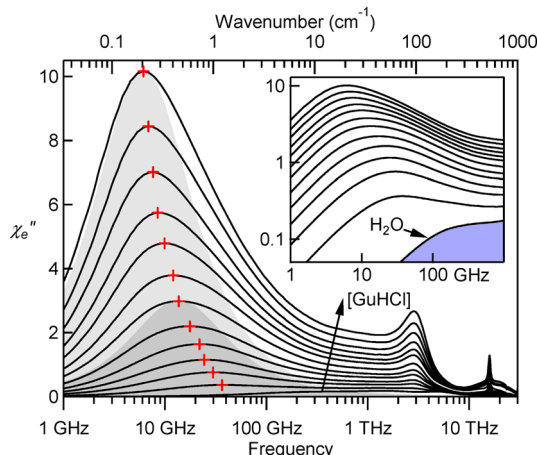

Figure 1. OKE spectra for aqueous guanidine hydrochloride (GuHCl) solution at 25 °C for concentrations from neat water to 7.35 M. The light and dark gray regions are Debye band shapes revealing the broadening of the (GuH$^+$) relaxation band at lower concentration. Crosses mark the position of the relaxation band maximum. The librational band appears at ca. 3 THz. The 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 $\approx$ 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 (section S3, Supporting Information), 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, $\tau_{OKE} = \omega_{peak}^{-1}$.

In Figure 2, τ_{OKE} is compared to viscosity along with the rotational relaxation time scale 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.

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, nonpolar 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 (section S2, Supporting Information). Hexadecane too has a simple spectrum, and in the mixture, the relaxation time scales 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 $\sim$90 GHz $\approx$ 1.8 ps) overlaps the librational mode (at $\sim$1 THz) but at low temperature is resolved as a Debye line shape (Figure 3a).
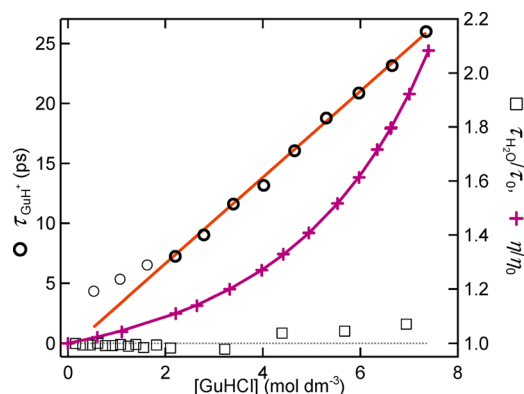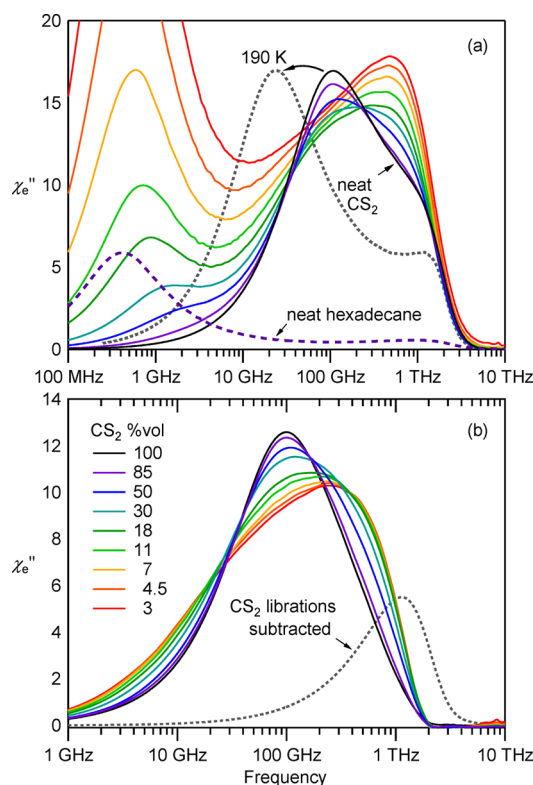

Figure 2. While the viscosity of aqueous GuHCl solution (crosses) increases nonlinearly with concentration (up to a factor of >2), the OKE rotational relaxation time scale for the GuH$^+$ ion (τ_{GuH^+}, circles) increases linearly above 2 M, and that of the water molecule measured by DRS[11] (squares)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

Figure 3. (a) OKE spectra at 20 °C for the CS$_2$:hexadecane mixture ranging from 3% (red) to 100% (black) volume ratio 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 (9× 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 time scale 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 the 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).

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 line shape (i.e., a simple exponential decay in time) with, in the neat liquid, a time constant of 392 ps.

To resolve the CS_2 relaxation contribution, the hexadecane contribution was fitted and then subtracted along with the CS_2 librational band (section S2, Supporting Information). The resultant spectra, principally the CS_2 relaxation, are shown in Figure 3b. 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 time scale with
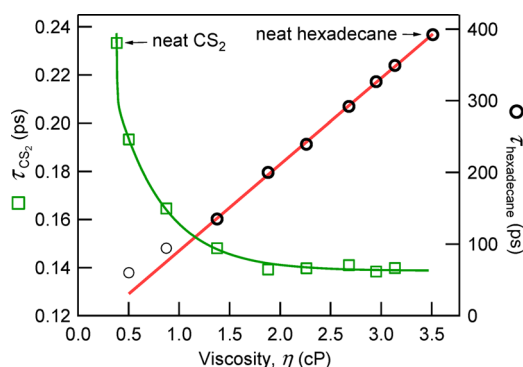

Figure 4. CS_2 time constant (reciprocal of $2\pi \times$ first moment of the relaxation band in Figure 3b) (squares) and Debye time constant for hexadecane relaxation (circles) vs viscosity for CS_2:hexadecane mixtures showing a linear correlation (SED behavior) (except at very low hexadecane concentration) for hexadecane relaxation and an anti-correlation for CS_2 relaxation. The seven highest data for hexadecane are fit by the line $120.5 \ (\pm 1.3) \times \eta - 30 \ (\pm 3)$.

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.

Despite this surprising behavior, the hexadecane relaxation time scale 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 $\tau_{rot} = V_{eff}\eta/k_BT + \tau_{rot}^0$. The fit in Figure 4 for hexadecane yields a gradient of $120.5 \ (\pm 1.3)$ ps cP^{-1}; hence, $V_{eff} = 120.5 \ k_BT$ ps cP$^{-1} = 488 \pm 5$ 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 nonexponential decay arising primarily from translation motion (section S3, Supporting Information). 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 time scale 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 nonpolar 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]

However, 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 nanometer range, below which local intermolecular forces dominate the translational mobility.

The exception here is hexadecane in a 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. However, 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 a widely used 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, while there are systems for which the application of SED is appropriate (e.g., nanometer-scale probe molecules used for studies in homogeneous solvents), the apparent observance of SED in other liquids should be treated with caution.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

(S1) Experimental details: optical Kerr-effect measurements and sample preparations. (S2) Optical Kerr-effect principles, time-domain data, details of fitting and analysis, and viscosity measurements. (S3) Calculation of the effect of clustering on OKE spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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