Relation between orientational correlation time and the self-diffusion coefficient of tagged probes in viscous liquids: A density functional theory analysis

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The usual explanation for the observed inverse relation between the orientational correlation time (τ_R) and the self-diffusion (D_S) of a tagged solute probe in a viscous liquid is in terms of the hydrodynamic relations which are known to have dubious conceptual validity for small molecules. Here, we present a microscopic derivation of the relation between τ_R and D_S. This derivation is based on the general ideas of the mode coupling theory, but uses the time-dependent density functional theory to obtain the torque–torque and force–force time correlation functions on the solute probe. Our analysis shows that the orientational correlation time (τ_R) is inversely proportional to the translational diffusion coefficient (D_0) of the solvent molecules. Thus, the viscosity dependence of orientational correlation time enters through the viscosity dependence of the translational diffusion (D_0). The same theoretical analysis also shows that the translational diffusion coefficient of the solute probe (D_S) is also proportional to the translational diffusion coefficient, D_0, of the solvent molecules. This result is in agreement with the recent computer simulation results which show that the product of τ_R and D_S is a weak function of the density (hence of the viscosity) of the liquid. The microscopic expressions provide explanation, in terms of the solute–solvent direct correlation functions, the reason for the sensitivity of orientational diffusion to solute–solvent interaction potential.

I. INTRODUCTION

Understanding correlations between the solvent viscosity, and the rotational and translational motions of a probe molecule, has been a subject of attention for many years.[1–9] Rotational relaxation has been extensively studied because it can be investigated by several experimental techniques, like dielectric relaxation, NMR, fluorescence depolarization, Kerr relaxation, solvation dynamics.[6,8] The rate of rotational relaxation is commonly explained by using the solvent viscosity dependence and the orientational correlation time, τ_R, is given by the well-known Debye–Stokes–Einstein (DSE) relation

$$\tau_R = \frac{C_R \eta v_s}{k_B T}, \tag{1}$$

where $k_B T$ is Boltzmann constant times the temperature (T), η is the viscosity of the liquid medium, v_s is the specific volume of the molecule, and C_R is a constant which is equal to 3 in the DSE theory, but usually found to be much smaller and is, therefore, often left as a fitting parameter. The rotational diffusion coefficient (D_R) is given by $D_R = 1/2\tau_R$. One finds that Eq. (1) provides a reasonable, although by no means perfect, description of the viscosity dependence of the observed rotational correlation time. Note that $C_R = 0$ is the prediction of the slip hydrodynamic boundary condition for a spherical rotor, which is unrealistic. At first this appears to be paradoxical because slip boundary condition is known to provide a satisfactory description of translation diffusion of small molecules. This was resolved by Hu and Zwanzig,[1] who showed that a reasonable value of τ_R for the rotation of a probe is obtained in most cases if the solute is approximated by a spheroid, which is the correct description of the shape of solute probes employed in experiments. Hu-Zwanzig calculation also gives $\tau_R/\eta = \text{constant}$.

The physical picture behind the hydrodynamic derivation of diffusion is that a tagged molecule diffuses due to its coupling with the natural currents of the liquid. In this picture, the small amplitude motions of the tagged molecule due to interactions with the surrounding molecules lead to no significant diffusion as the long-range natural currents are more effective in the long-time diffusion of the tagged molecule. Another uncertain aspect of this logic is the use of hydrodynamic boundary conditions employed to couple the solute's motion to the currents of the liquid. This physical picture behind rotational diffusion gets somewhat blurred, because now the molecule is made to rotate as a result of coupling to the same currents which give rise to torque on the rotor's surface. As a result, now the molecule can rotate without any hydrodynamic friction, which is known as the slip limit. We have already discussed that part of these difficulties were resolved by Hu and Zwanzig,[1] but some problems remain.

From a physical point of view, one would imagine that rotation of a probe molecule in a viscous liquid should be

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coupled to the structural relaxation of the surrounding solvent; that is, determined primarily by the local dynamics. The latter is determined largely by the translational diffusion coefficient (D_0), and also the structure, of the neighboring molecules. Thus, the rotational diffusion of a probe should be ideally correlated with the translational diffusion coefficient of the solvent molecules. We are, however, not aware of any such relation.

The translational diffusion of the same probe D_S can also be studied by tracer diffusion and many other experimental techniques. Now, the translational diffusion of the probe is also expressed in terms of solvent viscosity by invoking again the hydrodynamic relation between D_S and η

$$D_S=\frac{k_BT}{C_T\eta R}. \tag{2}$$

If one combines Eqs. (1) and (2) one obtains the following hydrodynamic prediction for the product of τ_R and D_S:

$$\tau_R D_S=\frac{C_R v_s}{C_T R}, \tag{3}$$

so that the said product does not depend on viscosity or any other dynamical property of the solvent, but only on the geometric properties of the solute. This constancy of $\tau_R D_S$ has been observed in recent computer simulations.[10] An example of this behavior has been shown in Fig. 6 of Ref. 6, where the product $D_S\tau_R$ is plotted against density for a wide range of density. In this simulation, the probe is a prolate ellipsoid and the solvent is a collection of Lennard-Jones spheres. It was interesting to note the plateau in the product $\tau_R D_S$ over a considerable variation of density. This could be taken as a confirmation of hydrodynamic expressions.

As discussed earlier, both translational and rotational motion of a small solute probe in a dense liquid is expected to be coupled to the structural relaxation of the surrounding solvent molecules and thus to the translational diffusion of the solvent molecules and the local structure. While the same is expected to dominate the viscosity in dense liquids also, one should indeed have a relation between the rotational and translational motion of a solute probe to the solvent viscosity. However, the reason behind this relationship between diffusions and viscosity can be entirely different from the one based on hydrodynamic arguments.

The problem is that we do not have a simple and transparent argument which provides these relationships from a microscopic theory. A microscopic theory should be able to derive Eq. (3), preferably by using the translational diffusion of the solvent as a variable. The theory should also be able to relate these diffusions with solvent viscosity. The objective of the present work is to show that such derivations are possible within the general framework of the mode coupling theory.[11] This work is partly motivated by our earlier work,[12] which showed that mode coupling theory can *quantitatively* explain the close relationship between the viscosity and friction. The second motivation comes from computer simulations, which shows that Eq. (3) indeed holds in the liquid density range with surprising accuracy.

The coupling between rotation and translation has been a subject of discussion recently in connection with solvation dynamics in restricted geometries. The first experimental paper to probe this connection was carried out by Vajda *et al.*,[13] who showed that the rate of solvation of a dipolar solute probe gets considerably reduced when the probe is confined within a cyclodextrin cavity. It has been proposed that this reduction is due to nonparticipation of the translational modes.[14] There is another, more subtle effect. If the translational mode gets quenched, then the rotational motion can also get severely quenched. A situation like this happens in the orientational motion of water molecules on the surface of an aqueous micelle or within a reverse micelle.[15,16] However, no microscopic theoretical study of this inter-relation between the translation and rotation has been carried out. In the absence of any such study, one always has to appeal to hydrodynamics and correlate the two via viscosity.

Experimental studies on supercooled liquids have found a significant deviation from the hydrodynamic prediction. Such deviations have been explained in terms of heterogeneities in the dynamics.[17–19] The existing explanation makes use of the linear viscosity dependence of rotational correlation time and the inverse viscosity dependence of translational diffusion coefficient of the probe. However, it would be more appropriate to correlate these quantities to the local diffusion coefficients of the solvent molecule.

Thus, to summarize, note that other than hydrodynamic arguments, there exists no microscopic argument of the viscosity dependence of the rotational time constant. In particular, we are not aware of any statistical mechanical derivation of Eq. (3), invoking spatial and time correlation functions. This is an objective of this paper. We present a microscopic derivation of Eq. (3), starting from time-dependent free-energy functional derived from the density functional theory. In a general sense, this is essentially a Ginzburg–Landau theory. The resulting expression is essentially a mode coupling theory result.

The organization of the rest of the paper is as follows. In the next section, we present a theoretical formulation for rotational dynamics. We do the same for translational diffusion in Sec. III. In Sec. IV, we discuss the theoretical results and also compare with existing simulations. Section V concludes with a brief discussion.

II. MICROSCOPIC EXPRESSION FOR ROTATIONAL RELAXATION TIME

The rotational relaxation time τ_R is related to the zero frequency rotational friction ζ_R by the usual expression

$$\tau_R=\frac{1}{2D_R}=\frac{1}{2}\ \frac{\zeta_R}{k_BT}. \tag{4}$$

A fully microscopic calculation of ζ_R is highly nontrivial and no such calculation for an ellipsoidal molecule has been carried out yet, except in the Enskog limit.[20] However, in a viscous liquid, this friction is expected to be dominated by the slow density relaxation. The friction can be expressed as a sum of two terms

$$\zeta_R=\zeta_{R,\mathrm{bin}}+\zeta_{R,\rho\rho}, \tag{5}$$

where $\zeta_{R,\mathrm{bin}}$ is the friction due to binary collisions while $\zeta_{R,\rho\rho}$ is the contribution due to density fluctuations. As mentioned earlier, in a viscous liquid, it is the latter that makes the dominant contribution. In the following we present a microscopic but simple derivation of the the latter friction.

Let us start by considering a very dilute solution of ellipsoids in a solvent of spherical molecules. This is perhaps the simplest possible system which can be used to study the viscosity dependence of orientational relaxation of the ellipsoids. Let us assume that $\rho_{\mathrm{ell}}(\mathbf{r,\Omega,t})$ denote the position $\mathbf{r}$, orientation $\mathbf{\Omega}$, and time t-dependent number momenta density of the ellipsoids and $\rho_s(\mathbf{r},t)$ denote the position and time-dependent number density of the solvent molecules. ρ_{ell} and ρ_s denote the average solute and solvent densities, respectively. The former does not enter the theoretical expressions derived below.

The relaxation of these densities can be described by using a molecular hydrodynamic theory of orientational relaxation described elsewhere. The molecular hydrodynamic equations are solved conveniently by Fourier and Laplace transforming them to the wave vector and frequency space (with wave vector $\mathbf{k}$ conjugate to position $\mathbf{r}$ and frequency z conjugate to time t). Since the details have been discussed elsewhere,[9] we shall just provide the essentials. We start by expanding the orientational density in the spherical harmonics,

$$\rho_{\mathrm{ell}}(\mathbf{k,\Omega},t)=\sum a_{lm}(\mathbf{k},t)Y_{lm}(\mathbf{\Omega}). \tag{6}$$

The experimentally observed orientational correlation functions are of two kinds: the collective and the single particle. The collective correlation functions are defined in the time domain by

$$C_{lm}(k,t)=\langle a_{lm}(-\mathbf{k},t=0)a_{lm}(\mathbf{k},t)\rangle. \tag{7}$$

Usually, by collective limit, one implies the $k=0$ limit of the above function. The single particle orientational correlation functions, on the other hand, are defined by

$$C_{lm}^{s}(t)=\langle Y_{lm}(\Omega_i(0)Y_{lm}(\Omega_i(t)\rangle, \tag{8}$$

where one considers the orientational dynamics of a single particle, modulated of course by interactions with all the other particles of the medium. In the present case, the two correlation functions approach each other because we consider only a very dilute solution of ellipsoids. In addition, we assume that the solvent has no orientational degrees of freedom.

The relaxation of the the orientational correlation functions depends on the torque and the force exerted by the surrounding solvent molecules. These torque and force, which act on a tagged ellipsoidal molecule at position $\mathbf{r}$ with orientation $\mathbf{\Omega}$ at time t, can be derived from the density functional theory, which gives the following general expression for the free-energy functional of an inhomogeneous system:[9]

$$\begin{aligned}\beta\mathcal{F}[\rho_{\mathrm{ell}}(t),\rho_s(t)]=&\int d\mathbf{r}\,d\mathbf{\Omega}\,\rho_{\mathrm{ell}}(\mathbf{r},\mathbf{\Omega},t)[\ln\rho_{\mathrm{ell}}(\mathbf{r},\mathbf{\Omega},t)-1]\\&+\int d\mathbf{r}\,\rho_s(\mathbf{r},t)[\ln\rho_s(\mathbf{r},t)-1]\\&-\frac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'\,d\mathbf{\Omega}c_{ls}(\mathbf{r}-\mathbf{r}',\mathbf{\Omega})\\&\times\delta\rho_{\mathrm{ell}}(\mathbf{r},\mathbf{\Omega},t)\,\delta\rho_s(\mathbf{r}',t)\\&-\frac{1}{2}\int d\mathbf{r}\,d\mathbf{r}'c_{ss}(\mathbf{r}-\mathbf{r}')\\&\times\delta\rho_{\mathrm{ell}}(\mathbf{r},t)\,\delta\rho_s(\mathbf{r}'t),\end{aligned} \tag{9}$$

where $\delta\rho_{\mathrm{ell}}(\mathbf{r},\mathbf{\Omega},t)=\rho_{\mathrm{ell}}(\mathbf{r},\mathbf{\Omega},t)-\rho_{\mathrm{ell}}/4\pi$ is the fluctuation in the position and orientation dependent number density $\rho_{\mathrm{ell}}(\mathbf{r},\mathbf{\Omega},t)$ and $\delta\rho_s(\mathbf{r},t)=\rho_s(\mathbf{r},t)-\rho_0$. Here, ρ_{ell} and ρ_0 are the corresponding average number densities. The direct correlation functions, $c_{ss}(\mathbf{r}-\mathbf{r}')$ and $c_{ls}(\mathbf{r}-\mathbf{r}',\mathbf{\Omega})$ are the second-order expansion coefficients in the expansion of the free-energy functional in the respective densities. Needless to say, we have truncated the free-energy expansion in Eq. (9) after the quadratic term in the density fluctuation.

We next assume, in the spirit of mode coupling theory, that the torque on a molecule is determined by the density fluctuations. The above density functional theory can be used to derive an expression for the torque. $\mathbf{N}(\mathbf{r},\mathbf{\Omega},t)$ is the torque on a tagged ellipsoid at $(\mathbf{r},\mathbf{\Omega},t)$. The procedure is simple and is well-documented.[9] One takes a functional derivative of the free energy given by Eq. (9) with respect to the space and orientation dependent density. When this derivative is set to zero and the resultant equation is solved for the equilibrium density, one can identify an effective potential energy. Torque is obtained by taking an angular gradient of this potential. The expression for the torque obtained by this procedure is given by[9]

$$\mathbf{N}(\mathbf{r},\mathbf{\Omega},t)=k_BT\nabla_{\mathbf{\Omega}}\int d\mathbf{r}'\;c(\mathbf{r}-\mathbf{r}',\mathbf{\Omega})\,\delta\rho(\mathbf{r}',t). \tag{10}$$

Note that the above expression for the torque provides a clear explanation of the coupling of the rotor's motion to the isotropic density fluctuation of the solvent. The orientational friction can now be given by Kirkwood's formula, which expresses the friction as an integral over the torque–torque time correlation function,[9]

$$\begin{aligned}\zeta_{R,\rho\rho}=&\frac{1}{2k_BT}\int_0^\infty dt\,\frac{1}{4\pi V}\int d\mathbf{r}\,d\mathbf{\Omega}\langle\mathbf{N}(\mathbf{r},\mathbf{\Omega},0)\\&\cdot\mathbf{N}(\mathbf{r},\mathbf{\Omega},t)\rangle,\end{aligned} \tag{11}$$

where $\langle ...\rangle$ involves averaging over the initial solvent configuration and also solvent dynamics when the position and the orientation of the solute probe are held fixed.

In the subsequent steps one writes the integral in the wave vector ($\mathbf{k}$) space, and expands both the direct correlation function and the density field in the spherical harmonics (in the framework where $\mathbf{k}$ is taken parallel to the z axis). Straightforward algebra leads to the following expression for the torque:

$$\mathbf{N}(\mathbf{r},\mathbf{\Omega},t)=\frac{1}{(2\pi)^3}(\nabla_\Omega Y_{lm}(\mathbf{\Omega}))\int d\mathbf{k}\,e^{i\mathbf{k}\cdot\mathbf{r}}c_{lm}(k)\,\delta\rho(\mathbf{k},\mathbf{t}), \tag{12}$$

where $\delta\rho(\mathbf{k},t)$ is the Fourier transform of $\delta\rho(\mathbf{r},t)=\rho(\mathbf{r},t)-\rho_0$, where ρ_0 is the average solvent density. $c_{lm}(k)$ is the lmth coefficient in the spherical harmonic expansion of the direct correlation function $c(k,\mathbf{\Omega})$ term which is the Fourier transform of the two particle $c(\mathbf{r}-\mathbf{r}',\mathbf{\Omega})$. The above expression for the torque is now substituted in Eq. (11). The subsequent steps involve an integration by parts and an integration over angles to obtain the following expression for the time-dependent friction:

$$\zeta_{R,\rho\rho}(t)=\frac{k_BT\rho_s}{16\pi^3}\int dk\,k^2\sum_{lm}l(l+1)c_{lm}^2(k)F(k,t). \tag{13}$$

In the above expression $F(k,t)$ is the dynamic structure factor or the intermediate scattering function of the liquid. This equation has the structure well-known in the mode coupling theory of liquid dynamics, although we have not come across this expression before. In dense liquids, most of the contribution to this integration comes from the intermediate wave number regime where the static structure factor of the liquid, $S(k)$, has a sharp peak. In this region, the dynamic structure factor or the intermediate scattering function, $F(k,t)$ can be given by the following simple expression:

$$F(k,t)=S(k)\exp(-D_0k^2t/S(k)), \tag{14}$$

where D_0 is the translational diffusion coefficient of the solvent molecules. If we substitute this expression in Eq. (13) for $\zeta_{R,\rho\rho}$, and carry out the integration over wave number k, we get the following expression for the friction:

$$\zeta_{R,\rho\rho}=\frac{k_BT\rho_s}{16\pi^3D_0}\int dk\,S(k)\sum_{lm}l(l+1)c_{lm}^2(k). \tag{15}$$

This equation can be recast in the form

$$\tau_RD_0=\frac{\rho_s}{32\pi^3}\int dk\,S(k)\sum_{lm}l(l+1)c_{lm}^2(k), \tag{16}$$

where we have used the relation between τ_R and the rotational diffusion coefficient, D_R. This expression has the nice feature that the terms on the right-hand side are purely static and determined solely by the local correlations. We are not aware of any prior derivation of such an expression.

We can now address the viscosity dependence of τ_R. Within mode coupling theory and with the same diffusive assumption for the dynamic structure factor, one can show that the collective part of viscosity is related to translational diffusion by the following relation:

$$D_0\eta=\frac{k_BT}{120\pi^2}\int dk\,k^2[S'(k)/S(k)]^2S(k). \tag{17}$$

Both τ_R and η are closely related to the translational diffusion coefficient of the solvent molecules because it is the latter which determines the rate of structural relaxation. We can use the last two equations to eliminate D_T, the translational diffusion coefficient, and relate the rotational relaxation time directly to viscosity. One can draw several additional conclusions regarding the viscosity dependence of τ_R. First, the rotational correlation time is directly proportional to viscosity which is inconsistent with the theoretical predictions. Second, if coupling of the rotational correlation time with viscosity enters through the coefficients $C_{lm}(k)$, if these coefficients are small, then the rotational correlation times could get decoupled from viscosity. Thus, when one changes the viscosity through variation of the solvent or the temperature, these coefficients also change, thus leading to a more complex dependence. This aspect has been addressed earlier by many, including Zwanzig.[1]

III. MICROSCOPIC EXPRESSION FOR THE SELF-DIFFUSION COEFFICIENT OF A TAGGED SOLUTE

The self-diffusion coefficient of the probe is related to the friction by the Einstein relation. The total friction on the probe can be decomposed into two parts: one is the binary or short time friction determined by the collision with the surrounding solvent molecules, while the second one is determined by structural relaxation. In viscous liquids, it is the second one which is important. An expression for this friction can be found by using the Kirkwood's formula, given in this case by

$$\zeta_{S,\rho\rho}=\frac{1}{3k_BT}\int_0^\infty dt\,\frac{1}{4\pi V}\int d\mathbf{r}\,d\mathbf{\Omega}\times\langle\mathbf{F}(\mathbf{r},\mathbf{\Omega},0)\cdot\mathbf{F}(\mathbf{r},\mathbf{\Omega},t)\rangle, \tag{18}$$

where $\mathbf{F}(\mathbf{r},\mathbf{\Omega},t)$ is the force on the solute probe at position $\mathbf{r}$, with orientation $\mathbf{\Omega}$ at time t. We obtain an expression for the force from the density functional theory; this is given by

$$\mathbf{F}(\mathbf{r},\mathbf{\Omega},t)=k_BT\nabla\int d\mathbf{r}'\,C(\mathbf{r}-\mathbf{r}',\mathbf{\Omega})\,\delta\rho(\mathbf{r}',t). \tag{19}$$

One next follows the same steps as in the previous section to obtain the following expression for the friction:

$$\zeta_{S,\rho\rho}=\frac{k_BT\rho_s}{6\pi^2D_0}\int dk\,k^2\sum_{lm}c_{lm}^2(k)S(k). \tag{20}$$

Note that the sum over l on the right-hand side of the above equation starts with $l=0$, while that for rotational friction the sum over l starts from $l=1$. Thus, the first term on the right-hand side of Eq. (20) is the isotropic term well-known in the mode coupling theory expression of the friction. One expects this first term to dominate in most cases.

In the subsequent steps we eliminate D_0 from the expressions of τ_R and ζ_S to obtain the following expression for the product τ_RD_S:

$$\tau_RD_S=\frac{8\pi}{3}\frac{\int dkS(k)\Sigma_{lm}l(l+1)c_{lm}^2(k)}{\int dk\,k^2\Sigma_{lm}c_{lm}^2(k)S(k)}. \tag{21}$$

The above equation is an important result of this work. This provides a microscopic relation between the rotational time and the self-diffusion of a tagged probe in dense liquids.

Amplitude of rotational friction clearly depends on the spherical harmonic coefficients, $C_{lm}(k)$, in addition to the translational diffusion coefficient of the solvent. Unfortunately, reliable expressions for $C_{lm}(k)$ are hard to obtain. Approximate analytical forms are available for two model systems: dipolar hard spheres and a neat liquid of ellipsoids.[9,21,22] Nevertheless one can easily see the difference in the dependence of the rotational friction on the intermolecular potential from that of translational friction. Another rather surprising result is that the rotational friction is less local than the translational friction.

IV. RESULTS AND DISCUSSION

The main results of this paper are given in Eqs. (13), (16), and (21). Although no numerical study of these expressions has been carried out yet, one can draw several conclusions/conjectures from the nature of the above expressions. Below, we summarize our main conclusions.

(1) We have established that the orientational relaxation time of the solute probe is coupled primarily by the translational diffusion coefficient of the solvent. The clean separation between the static and dynamic terms is a consequence of the form assumed for $F(k,t)$, as given by Eq. (14). In highly viscous liquids, this form will break down.

(2) If one is changing the transport properties by increasing the pressure or lowering the temperature, then Eq. (21) suggests that there can be a small variation in the product $\tau_R D_S$. However, the product $\tau_R D_0$ can show a greater variation and should increase with increase of pressure or lowering of temperature. Thus, one might observe a viscosity dependence of τ_R which is even *stronger* than η. This can be observed only in highly viscous liquids.

(3) The above equations suggest an interesting density (or viscosity) dependence of the product $\tau_R D_S$. At low density or viscosity, we need to include the binary contribution both to the rotational and the translational friction, and the binary term is the dominant one at low densities. Now, as the density is increased from low values, the increase in τ_R is slower than the increase in D_S. So, the product $\tau_R D_S$ will first decrease with density. As one enters the liquid density, the product may vary slowly with density, as the two opposing trends may cancel each other. This is the region where hydrodynamic expression may appear to be valid. However, as density is further increased and we enter the viscous liquid regime, the binary contribution becomes negligible and we can find the product $\tau_R D_S$ again increase with density, pressure, or viscosity. It is interesting to note that these three domains have indeed been observed in recent simulations.[10]

V. CONCLUSION

In this article we have presented a theoretical study of correlations between viscosity, rotational and translational diffusion in dense liquids. We have shown that one can explain some of the experimental and simulation results without recourse to hydrodynamics. The latter is unsatisfactory on several counts, the most important being the conceptual difficulty one faces in accepting viscosity as the main variable to describe rotation of a small probe. We have argued the local structural relaxation of the solvent as the main determinant in the rotational and translational motions of tagged solutes. The theory suggests an alternative explanation for the constancy of the product $\tau_R D_s$, often observed in experiments.

As mentioned in the Introduction, this coupling between rotational and translational motions could have direct relevance in many experimental measurements. One currently active area where it is so is the dynamics in restricted geometries.[14,16] In such systems the translational motion of the solvent molecules can be restricted, which in turn can affect the rotational motion of either the probe or the solvent molecules, or both. In fact, the quenching of translational motion has been offered as a possible reason for the observed slow solvation dynamics in aqueous cyclodextrin cavities.[15] Other examples are motions within reverse micelles or at the surface of aqueous micelles.[16] In these systems both rotational and translational motions are found to exhibit a very slow decay, the origin of which is not clearly understood yet, but quenching of translational motion has been proposed as a plausible mechanism.[14]

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