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Nuclear magnetic resonance relaxometry as a method of measuring translational diffusion coefficients in liquids

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By application of the field-cycling technique, we measure the dispersion of the ^{1}H nuclear magnetic resonance (NMR) spin-lattice relaxation time $T_1(\omega)$ for a series of molecular liquids. We demonstrate that such NMR relaxometry studies can be used for determining diffusion coefficients. A broad frequency range of 10 kHz–20 MHz is covered. By scanning $T_1(\omega)$ one directly probes the spectral density of the diffusion processes. The value of the diffusion coefficient D can be determined from a linear dependence of the ^{1}H spin-lattice relaxation rate on the square root of the frequency at which it is measured. The power of this method lies in its simplicity, which allows one to determine $D(T)$ independently of the diffusive model. The results obtained are in very good agreement with those of field gradient NMR methods.

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Nuclear magnetic resonance (NMR) is a phenomenon that gives rise to a variety of specific experimental methods which are very valuable as sources of information on dynamical properties of molecular systems. In recent decades NMR field gradient diffusometry has became the key method of measuring translational diffusion coefficients D in liquids [1]. In order to probe the translational motion the sample is placed in an inhomogeneous magnetic field characterized by a linear, well-controlled field gradient. The position of a nucleus possessing a spin (an NMR-active nucleus) is monitored by changes in its Larmor frequency (precession frequency) which depend on the location of the traced nucleus. The range of D accessible by field gradient NMR methods is 10^{-6}–10^{-14} m^2 s^{-1} [1,2]. The higher bound of D refers to diffusion in gases while the lower one corresponds to moderately viscous (supercooled) liquids.

In this paper we demonstrate, focusing on liquids, that ^{1}H NMR relaxometry can be treated as a method complementary to field gradient diffusometry. The idea of NMR relaxation experiments is as follows [3,4]. First, the sample is polarized in a strong external magnetic field. The generated magnetization is proportional to the difference in the equilibrium populations of the ^{1}H Zeeman quantum states determined by the Boltzmann distribution. Then the field is switched to a lower value (relaxation field B_{rel}) and the energy levels repopulate according to the new equilibrium conditions. As a result the ^{1}H magnetization decreases in time, reaching eventually the value determined by the lower field B_{rel}. The magnetization decay is in most cases exponential with a time constant referred to as the spin-lattice relaxation time T_1. The spin transitions are induced by stochastic fluctuations of magnetic dipole-dipole interactions between pairs of protons (this is in most cases the dominating relaxation mechanism), and one has to distinguish between proton sites on the same molecule (intramolecular) and on different molecules (intermolecular). In consequence, the measured value of the relaxation rate R_1 ($R_1 = 1/T_1$) is the sum of two contributions resulting from intramolecular and intermolecular dipolar interactions, respectively [3]:

$$R_1(\omega) = R_{1,\mathrm{intra}}(\omega) + R_{1,\mathrm{inter}}(\omega), \tag{1}$$

where $\omega = \gamma_{\mathrm{H}} B_{\mathrm{rel}}$ (γ_{H} is the proton gyromagnetic factor). The intramolecular relaxation is associated with molecular rotation changing the orientation of the vector connecting the interacting nuclei (within a molecule) with respect to the direction of the external magnetic field. The relaxation rates depend on the spectral density of these fluctuations (as well as on the dipolar interaction strength). In the case of intermolecular relaxation the dipolar interactions are mediated by the relative translational motion of the molecules, which leads not only to fluctuations of the orientation of the internuclear axis, but also to changes in their separation, as reflected by the intermolecular dipolar correlation function $C_{\mathrm{inter}}(t)$ [3,5,6]:

$$C_{\mathrm{inter}}(t) \propto \left\langle \frac{Y_m^{2*}(\Omega(t))}{r^3(t)} \frac{Y_m^2(\Omega(0))}{r^3(0)} \right\rangle. \tag{2}$$

Here, the spherical harmonics $Y_m^2(\Omega)$ describe the molecular orientation via the Euler angle Ω, while r is the interspin distance. For isotropic liquids the rotational and translational dynamics averages the dipole-dipole interactions to zero. For dipolar relaxation of nuclei with spin quantum number $\frac{1}{2}$ the intermolecular relaxation rate $R_{1,\mathrm{inter}}(\omega)$, measured at the angular frequency $\omega = 2\pi\nu$, is related to the intermolecular spectral density J_{inter} [which is a Fourier transform of the correlation function $C_{\mathrm{inter}}(t)$] in a simple way according to the well-known relaxation formula [3]

$$R_{1,\mathrm{inter}}(\omega) = \frac{3}{10} N \left(\frac{\mu_0}{4\pi}\gamma_{\mathrm{H}}^2 \hbar\right)^2 [J_{\mathrm{inter}}(\omega) + 4J_{\mathrm{inter}}(2\omega)], \tag{3}$$

where N is the proton density (number of protons per unit volume). This number can be obtained from the relation $N = nN_A\rho/M_{\mathrm{mol}}$, where M_{mol} is the molecular mass, ρ is the density of the liquid, n is the number of hydrogen atoms per molecule, and N_A is the Avogadro number. Thus by varying the relaxation field the spectral density is scanned.

Until recently, field-dependent relaxation experiments had not been routinely possible. Due to the recent commercial

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availability of STELAR NMR field-cycling (FC) spectrometers, which cover about three orders of magnitude in the frequency (10 kHz–20 MHz for ^{1}H), NMR relaxometry gained new momentum [4,7]. The FC technique employs repetitive changes in the magnetic field: the external magnetic field is switched from a polarization field to a relaxation one and back to a high detection field. The measured frequency dependence of the spin-lattice relaxation rate $R_1 = T_1^{-1}$ is referred to as relaxation dispersion. An expression analogous to Eq. (3) can be written for the intramolecular relaxation rate $R_{1,\text{intra}}(\omega)$, but including intramolecular spectral densities that are associated with molecular rotation [3,7]. Thus the key dynamical processes, translation and rotation, can be monitored, in principle, with ^{1}H NMR relaxometry simultaneously, which is a unique and great advantage of this method, as shown in [7,8].

The rotational dynamics of a liquid can be probed by other methods, for instance dielectric spectroscopy (DS) [9]. The DS spectral density obtained from the imaginary part of the complex permittivity via $J_{\text{DS}}(\omega) = \varepsilon''/(\Delta\varepsilon\omega)$, where $\Delta\varepsilon$ is linked to the static dielectric constant ε_s [$(\varepsilon_s - \varepsilon_\infty) = \Delta\varepsilon$, where ε_∞ is the high-frequency permittivity], is often modeled by a Cole-Davidson spectral density which reflects its non-Lorentzian character. It gives as a limit a Lorentzian spectral shape that corresponds to an exponential correlation function (force-free isotropic tumbling). As dielectric spectroscopy is indifferent to translational motion, a comparison between NMR and DS results is of great value for differentiating between the contributions to the ^{1}H relaxation associated with rotation and translation. Recently, we have compared results of FC ^{1}H NMR relaxometry and DS for several viscous liquids such as glycerol [5,10]. ^{1}H NMR relaxation dispersion data compared with the DS results show a low-frequency excess contribution. To confirm its intermolecular (translational) origin, a series of ^{1}H NMR relaxation experiments for isotopically diluted systems (for instance glycerol-h_5 dissolved in glycerol-d_8) has been performed (for a full account see [11]). In Fig. 1 we show that the low-frequency contribution becomes progressively suppressed for a decreasing concentration of the ^{1}H-containing molecules. As ^{1}H-^{2}H dipole-dipole interactions are much weaker than those between proton pairs (^{1}H-^{1}H), this observation gives an ultimate proof of the intermolecular origin of the excess relaxation contribution. The intramolecular relaxation dispersion (obtained by extrapolating the relaxation data to the zero-concentration limit of glycerol-h_5) and the dielectric spectral density shapes are essentially identical as in both cases the rotational dynamics is solely probed. In conclusion, the dilution experiment shows that there is a considerable time scale separation of inter- and intramolecular relaxation contributions.

Different motional models have been applied to quantitatively describe the translational motion in condensed matter [12]. A closed form expression for the intermolecular correlation function referred to as the hard-sphere force-free diffusion model has been derived in [5,6]:

$$C_{\text{inter}}(t) = 72\frac{1}{d^3}\int_0^\infty \frac{u^2}{81 + 9u^2 - 2u^4 + u^6}\exp\left(-\frac{u^2 t}{\tau_{\text{trans}}}\right)du, \tag{4a}$$

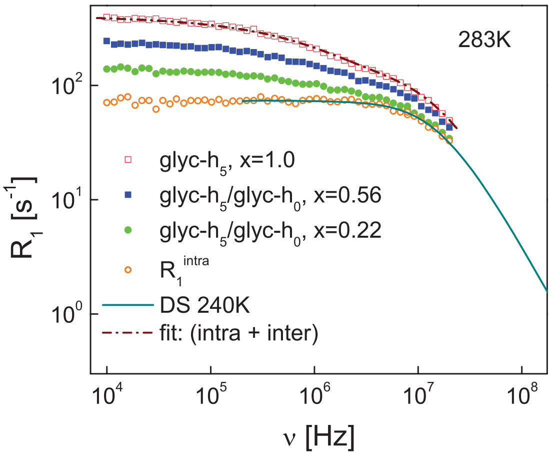

FIG. 1. (Color online) ^{1}H relaxation dispersion data for glycerol-h_8 and glycerol-h_5–glycerol-h_0 mixtures with a mole fraction $x = 100\%, 56\%, 22\%$, and 0% (extrapolated) of glycerol-h_5. Dashed-dotted line, fit in terms of the model presented in [8]. In the last case the low-frequency contribution disappears and only the intramolecular relaxation part (associated solely with rotational dynamics) remains. For comparison the dielectric spectral density is included (solid line). As it well agrees with the relaxation dispersion for $x = 0\%$ the translational origin of the low-frequency relaxation contribution is again confirmed.

which leads to the spectral density [8]

$$J_{\text{inter}}(\omega) = 72\frac{1}{d^3}\int_0^\infty \frac{u^2}{81 + 9u^2 - 2u^4 + u^6}\frac{u^2\tau_{\text{trans}}}{u^4 + (\omega\tau_{\text{trans}})^2}du, \tag{4b}$$

where u is an integration variable. This model assumes that the interacting nuclei are placed in the centers of the molecules that undergo Fick diffusion (force-free) with a uniform distribution of the molecules (treated as hard spheres) outside the distance of closest approach, d. The correlation time τ_{trans} is defined as $\tau_{\text{trans}} = d^2/D_{12}$, where D_{12} is the relative translational diffusion coefficient defined as the sum of self-diffusion coefficients of the participating molecules (thus for identical molecules it is twice larger than the self-diffusion coefficient, $D_{12} = 2D$). It has been shown by computer simulations that the effects of structural correlation present in liquids affect the intermolecular correlation function [13]. In addition, the intermolecular dipolar interactions are not only mediated by the translational motion, they are also affected by the molecular tumbling if the interacting nuclei were not placed in the molecular centers; this is referred to as eccentricity effects [14,15]. As we are going to extract the diffusion coefficients from the low-frequency range of the relaxation dispersion which corresponds to long times (via the inverse Fourier transform relationship) these effects become irrelevant [13,16,17]. For long times the intermolecular correlation function $C_{\text{inter}}(t)$ follows a power law $\propto t^{-3/2}$ that is characteristic of free diffusion. This time power law implies the form of the low-frequency expansion of the corresponding spectral

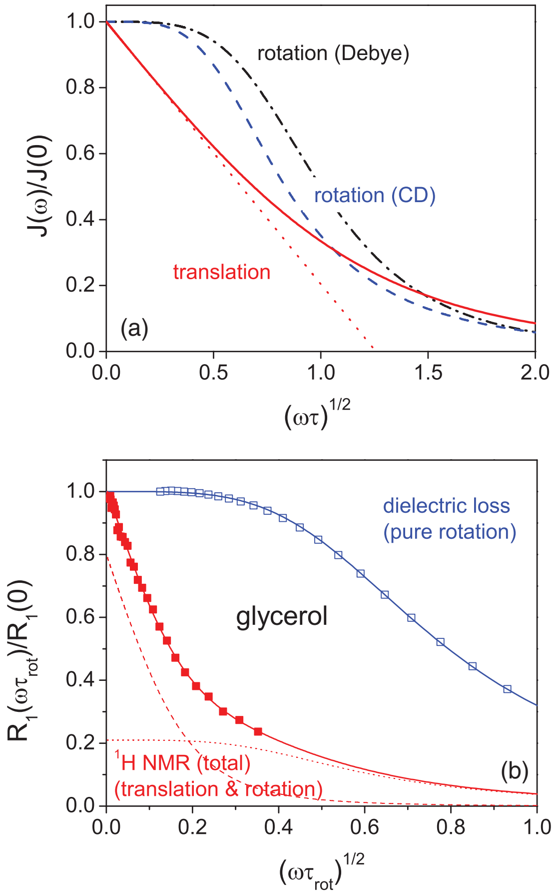

FIG. 2. (Color online) (a) Low-frequency behavior of the translational spectral density for the hard-sphere force-free model [5,6] compared with those of rotational spectral densities modeled as Debye and Cole-Davidson functions; dotted straight line, the limiting linear dependence predicted by Eq. (2). (b) Normalized ^{1}H NMR relaxation rate R_1 and dielectric spectral density for glycerol as functions of $\sqrt{\omega\tau_{\text{rot}}}$. The decomposition of the ^{1}H relaxation dispersion into intermolecular (dashed) and intramolecular (dotted) parts [8] shows that the first one controls the low-frequency shape of the entire relaxation curve.

density [5,12,18–21]:

$$J_{\text{inter}}(\omega) = a - b\sqrt{\omega}. \tag{5}$$

This expansion applies when $\omega\tau_{\text{trans}} < 1$. The seminal fact is that the constant b depends only on the diffusion coefficient D; it does not include any details of the diffusion model [12,17,21]. Besides the very simple mathematical formulation, which makes the task of determining the diffusion coefficient values straightforward, an important consequence of this relation is that for the intermolecular relaxation contribution there is no frequency-independent low-field region. This is illustrated in Fig. 2(a) where the intermolecular spectral density (obtained from the hard-sphere force-free model) is compared with Cole-Davidson and Debye (Lorentzian) spectral densities describing intramolecular relaxation associated with rotational motion, both plotted as functions of $\sqrt{\omega\tau}$ (τ denotes here the characteristic correlation time; it has been set as $\tau_{\text{trans}} = \tau_{\text{rot}} = \tau$.) While J_{inter} in the low-frequency range shows the linear dependence of Eq. (5), the intramolecular spectral density J_{intra} follows a Gaussian-like limiting dependence; for a Debye function (which is a special case of the Cole-Davidson function) one gets $J_{\text{intra}} \propto [1 - (\omega\tau_{\text{rot}})^2]$. Thus, from the low-frequency shape of the spectral density (relaxation rate) one can clearly distinguish between rotational and translational dynamics. To confirm this theoretically predicted feature we compare in Fig. 2(b) the ^{1}H relaxation dispersion $R_1(\omega)$ for glycerol with the corresponding DS results, both plotted as functions of $\sqrt{\omega\tau_{\text{rot}}}$. One sees that the limiting low-frequency behavior of $R_1(\omega)$ is indeed linear (it is determined by the translational contribution) whereas the DS results show a different frequency dependence.

The translational diffusion coefficient can be obtained from the model-independent relation $b = \pi/9D^{3/2}$. This implies [in combination with Eq. (3)] that for $\omega\tau_{\text{trans}} < 1$ the relaxation dispersion follows the relation

$$\begin{aligned} R_1(\nu) &\cong R_1(0) - B\sqrt{\nu} \\ &= R_1(0) - N\left(\frac{\mu_0}{4\pi}\gamma_{\text{H}}^2\hbar\right)^2\left(\frac{\sqrt{2}+8}{30}\right)\left(\frac{\pi}{D}\right)^{3/2}\sqrt{\nu}, \end{aligned} \tag{6}$$

where the intramolecular contribution has been included into $R_1(0)$ as there is no visible dispersion of the intramolecular relaxation in the linear range of the intermolecular contribution. The fact that the intramolecular relaxation contribution can be included into $R_1(0)$ is ensured by the relationship between the rotational and translational correlation times. For the idealized case of mono-atomic molecules modeled as hard spheres with the nucleus placed in the molecular center, it has been theoretically predicted that $\tau_{\text{trans}}/\tau_{\text{rot}} = 9$ [3]. Investigating a variety of liquids, we have found that this ratio is considerably larger (40–70) [10] (which makes the time scale separation of these two processes even more easily discernible, as is also seen in Fig. 1 for glycerol). As a result, the diffusion coefficient can be straightforwardly calculated from the slope B (which contains only the spin density N and the diffusion coefficient D) of the limiting linear dependence of $R_1(\nu)$ on $\sqrt{\nu}$. We wish to stress that, although relaxation dispersion data contain both the intramolecular and intermolecular components (which makes them a unique source of information about the rotational and translational motion at the same time), for determining the translational diffusion coefficient there is no need to separate these contributions.

Although the feature of the low-frequency intermolecular relaxation dispersion encoded in Eq. (6) has been known for years, its advantages have not been appreciated so far. The relationship has been used to determine the diffusion coefficient for paramagnetic species in solutions [17]. In all cases the focus was on the dynamics of the paramagnetic molecules and the electron spin relaxation. In fact, the relationship of Eq. (6) was once applied to determine the diffusion coefficient of molecular liquids a long time ago [19]; however, this possibility was not, to our knowledge, further exploited until now. The reason likely lies in experimental difficulties—field-dependent relaxation studies have become routinely available only recently.

We have collected ^{1}H spin-lattice relaxation dispersion data for several liquids. In Fig. 3, as an example, the ^{1}H relaxation data for xylitol [$\text{HOCH(CH}_2\text{OH)}_3\text{CH}_2\text{OH}$] obtained in a broad

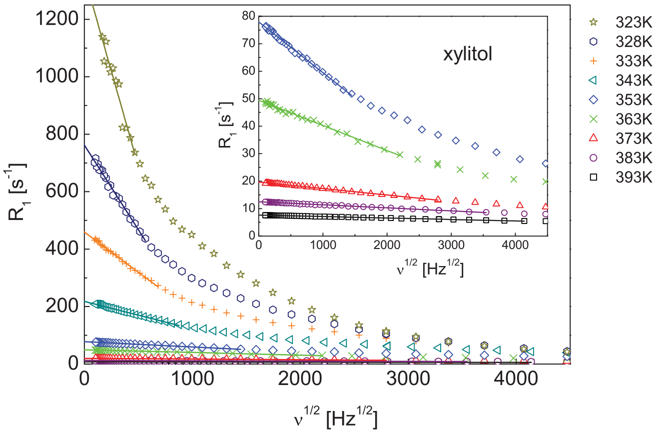

FIG. 3. (Color online) ^{1}H relaxation dispersion of the liquid xylitol plotted as a function of $\sqrt{\nu}$; the slope of the linear part at low frequencies yields the diffusion coefficient $D(T)$ [cf. Eq. (6)]; the inset shows enlarged high-temperature data.

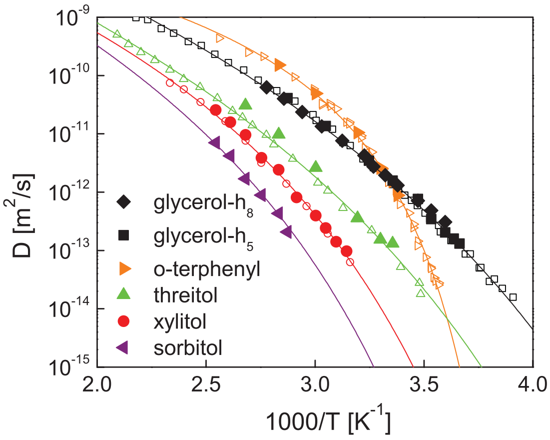

FIG. 4. (Color online) Translational diffusion coefficient D as obtained from ^{1}H NMR relaxometry (full symbols) for several liquids versus the reciprocal temperature; for comparison data from field gradient NMR (open symbols) are displayed [22–24]; the data are interpolated via the Vogel-Fulcher-Tammann expression [10].

temperature range are plotted against $\sqrt{\nu}$. The linear range of this dependence progressively extends to higher frequencies when the motion becomes faster (higher temperatures). The values of the diffusion coefficients extracted from the linear part are compared with those from NMR field gradient diffusometry [22–24] in Fig. 4. The results follow the Vogel-Fulcher-Tammann expression [10] as is typical of viscous liquids. A very good agreement between NMR relaxometry and diffusometry is reached, encouraging us to explore further the potential of ^{1}H NMR relaxometry by applying it to other systems. The results for other liquids also are in a very good agreement with those of field gradient diffusometry. It is worth mentioning that recently we have applied a full relaxation theory combined with the force-free hard-sphere diffusion model to reproduce the whole relaxation dispersion including the determination of the rotational time constants—cf. Fig. 1 [8,11].

As far as fast diffusional motion is concerned, the limit of NMR relaxometry is determined only by the fact that a perceptible (beyond the experimental inaccuracy of the FC technique) relaxation dispersion has to be seen in the accessible frequency range (up to 20 MHz). Using conventional NMR spectrometers operating at higher frequencies (say up to 600 MHz), this range can be considerably extended. Nevertheless, NMR relaxometry loses its sensitivity for fast diffusion processes of the order of water diffusion (10^{-9} m^2/s). The slow diffusion limit is determined by two factors. The first one is that using this type of spectrometer one cannot measure relaxation times shorter than 1 ms. In the low-field range the relaxation time decreases when the correlation times becomes longer, eventually reaching this limit. The second limitation is that the linear range of the relaxation dispersion is observed when the condition $\omega\tau_{\text{trans}} < 1$ is fulfilled. This implies that to be able to detect the linear part of the relaxation dispersion at the low-frequency limit of 10 kHz, the correlation time τ_{trans} must not be longer than approximately 5×10^{-6} s. Using the relation $\tau_{\text{trans}} = d^2/2D$ introduced in the force-free hard-sphere model, where d defined as the distance of closest approach is close to the molecular diameter, one can estimate the upper limit of the accessible values of the diffusion coefficient. For a molecule of diameter of the order of 3 Å one reaches $D \cong 10^{-14}$ m^2/s, which is at the limit of field gradient NMR diffusometry. We have thus demonstrated that ^{1}H NMR relaxometry can serve as a highly advantageous method of determining values of diffusion coefficients in a broad range. Taking into account the simplicity of the mathematical operations required, one can say that the diffusion coefficients are accessible in a (almost) direct way. The proposed method of determining diffusion coefficients can be used in a variety of areas—from industrial applications (such as, for instance, probing oil properties) to various research fields. Although we concentrated on ^{1}H relaxometry, other nuclei, such as, for instance ^{19}F, can also be exploited, which enlarges its potential. Nevertheless, when other (than dipole-dipole) relaxation mechanisms are of importance (for instance, hyperfine interactions for paramagnetic systems), Eq. (6) has to be modified according to a relaxation theory appropriate for the system of interest.

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