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A study of the Debye–Stokes–Einstein law in supercooled fluids

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Abstract. The reorientation of a nearly spherical paramagnetic tracer dissolved in supercooled *o*-terphenyl is studied by electron spin resonance in the range $200 \text{ K} < T < 370 \text{ K}$. For $T > 300 \text{ K}$ the rotational correlation time τ_2 follows the Debye–Stokes–Einstein law. On decreasing the temperature, the rotational motion of the probe and the viscosity η decouple. In particular, in the region around $T = 290 \text{ K}$ it is found that $\tau_2 \propto (\eta/T)^\xi$ with $\xi = 0.28 \pm 0.04$.

1. Introduction

The diffusion of macroscopic objects in a fluid is well accounted for by the Stokes–Einstein (SE) and the Debye–Stokes–Einstein (DSE) laws, pertaining to the translational and the rotational diffusion, respectively [1, 2]. In particular, for a spherical molecule the DSE law takes the form

$$\tau_l = \frac{6}{l(l+1)} \frac{v\eta}{kT}. \quad (1)$$

τ_l is the rotational correlation time of the tagged particle, namely the area under the normalized correlation function of the spherical harmonic $Y_{l,0}$. k and T are the Boltzmann constant and the temperature, respectively. v is related to both the molecular effective volume and the surface boundary conditions and η is the shear viscosity.

Both the SE and the DSE laws follow from hydrodynamics and the fluctuation-dissipation theorem. However, it is well known that in fluids having low viscosities they reproduce fairly well the experimental data down to *molecular* length scales. The robustness of the above laws in a sense motivated the belief that they are generally true, especially in the weaker form stating that the diffusion constants (or, equivalently, the correlation times) are proportional to η . Anyway, since molecules may diffuse also in solid host matrices, a breakdown of the SE and DSE laws may be anticipated in fluids with high viscosity.

In the last few years a number of experimental works provided evidence of a failure of both the DSE and the SE laws in polymers [3, 4] and supercooled molecular fluids [5, 6, 7]. Inspection of the available data points to a new diffusive regime which sets in close to the critical temperature T_c predicted by the mode-coupling theory of the glass transition [8]. In that regime the viscosity and the diffusion are partially decoupled, the latter being much

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less temperature dependent. The decoupling is well described by power laws. In particular, the DSE law takes the fractional form (FDSE)

$$\tau_l = C_l \left(\frac{\eta}{T} \right)^\xi \quad 0 \leq \xi \leq 1. \quad (2)$$

A number of promising models of the decoupling have been proposed [2, 9, 10]. However, the fractional DSE and SE laws have not been explicitly derived yet. A possible interpretation of the decoupling in terms of free volume is not consistent with the experiment [3].

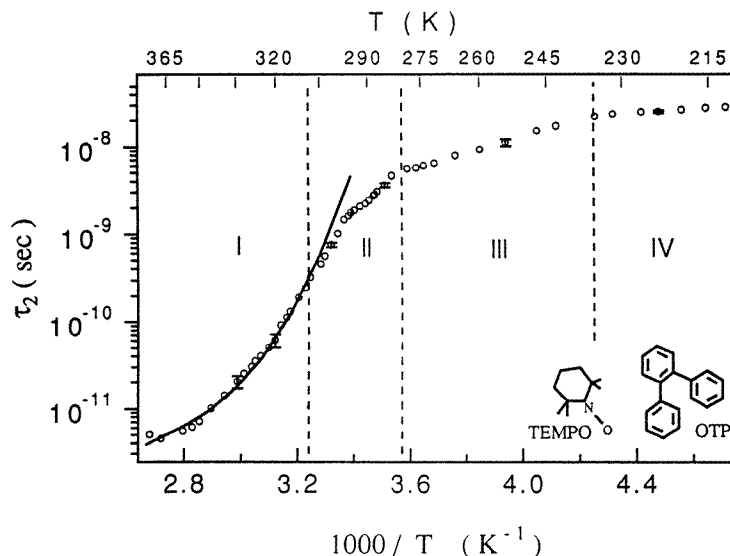


Figure 1. The temperature dependence of the rotational correlation time of TEMPO τ_2 . The solid line is the best fit with the DSE law.

Recently, our laboratory reported on an electron spin-resonance (ESR) investigation of the rotational motion of molecular tracers in the glass transition region of *o*-terphenyl (OTP) [11]. The present paper extends the study at higher temperatures and yields new evidence of the FDSE law. A preliminary note of this work was published elsewhere [12].

2. Experimental details

Samples were prepared by dissolving TEMPO radical (2, 2, 6, 6 tetramethyl-piperidin-1-oxyl, 98% Aldrich) in as-received OTP (99% Aldrich, $T_g = 243$ K) in a concentration of 10^{-3} mol l^{-1} . The molecular structures of TEMPO and OTP are shown in figure 1. Their average Van der Waals radii r are comparable, being $r_{OTP} = 0.37$ nm [5] and $r_{TEMPO} \cong 0.34$ nm. The magnetic parameters of TEMPO were drawn by careful analysis of the ESR powder spectrum of TEMPO. τ_2 -values were drawn from numerical simulation of the ESR lineshape assuming isotropic jump diffusion. Details on the related theory, sample preparation and ESR spectrometer may be found elsewhere [11].

3. Results and discussion

Figure 1 shows the temperature dependence of the rotational correlation time of TEMPO τ_2 in the range $200 \text{ K} < T < 370 \text{ K}$. Four different regions are identified.

In region I ($T > 308 \text{ K}$) the data are well described by the DSE law. From equation (1) with slip boundary conditions (expected for the small and nearly spherical TEMPO molecule), it is found that the apparent average radius of TEMPO is $r_{TEMPO}^* \cong 0.26 \text{ nm}$ to be compared with the average Van der Waals radius $r_{TEMPO} \cong 0.34 \text{ nm}$.

In region II ($280 \text{ K} < T < 308 \text{ K}$), which includes the so-called critical temperature $T_c = 290 \text{ K}$ predicted by the mode-coupling theory of the glass transition [8], τ_2 and the viscosity decouple. In this region the values of the correlation time τ_2 do not depend on the particular model of the rotational motion of TEMPO being assumed in the numerical simulation of the ESR lineshape. In fact, if $\tau_2 \sim 10^{-9} \text{ s}$, the ESR linewidth is mainly related to the areas $J_{p,q}(0)$ under the correlation functions of the elements of the rotation Wigner matrix of rank 2 $D_{p,q}^2$, i.e. $C_{p,q}(t)$ ($|p|, |q| \leq 2$). Smaller contributions come from the Laplace transform of $C_{p,q}(t)$, $J_{p,q}(\nu)$ evaluated at the Larmor frequency $\nu_0 \sim 10^{10} \text{ Hz}$ and the hyperfine frequency $\nu_I \sim 10^8 \text{ Hz}$. To substantiate the above statement, we studied the dependence of τ_2 -values on the form of $J_{p,q}(\nu)$ by assuming a Cole–Davidson form:

$$J_{p,q}(\omega) = \frac{1}{5} \frac{\sin[\beta \arctan(\omega\tau_{CD})]}{\omega(1 + (\omega\tau_{CD})^2)^{\beta/2}} \quad \text{with } \tau_2 = \beta\tau_{CD}. \quad (3)$$

Table 1 summarizes the results and shows that for some representative points taken from region II τ_2 is largely independent of the parameter β which is set to $\beta = 1$ in all the simulations. We note that in the time domain the Cole–Davidson form corresponds approximately to a stretched exponential with parameter β .

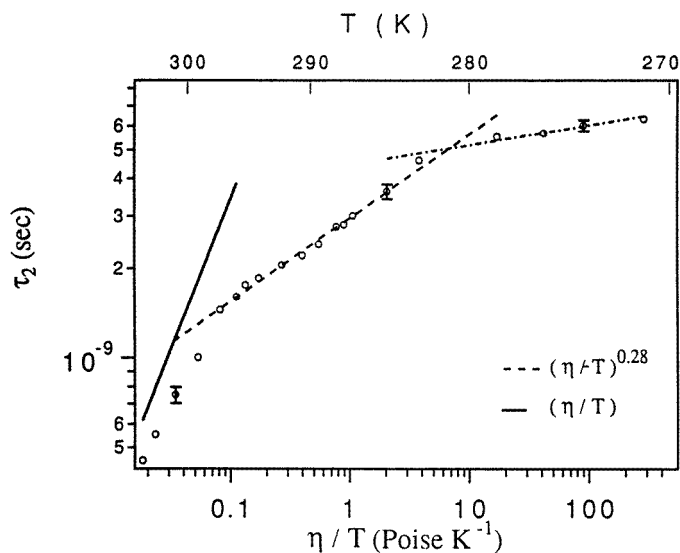


Figure 2. Region II of figure 1 ($280 \text{ K} < T < 308 \text{ K}$). Continuous line: extrapolated DSE law from region I; dashed line: best fit with the FDSE law; chain line: Arrhenius law fitting the data in region III.

Table 1. Dependence of τ_2 (in ns) on the Cole–Davidson parameter in region II.

T (K)	$\beta = 1$	$\beta = 0.6$	$\beta = 0.1$
288.1	2.75	2.85	2.65
290.5	2.20	2.30	2.25
293.8	1.85	1.90	1.80
297.0	1.45	1.47	1.40

The τ_2 -data in region II are compared with the viscosity in figure 2. Using the FDSE law (equation (2)) yields the best-fit values $C = (2.94 \pm 0.13) \times 10^{-9}$ and $\xi = 0.28 \pm 0.04$.

The crossover between the regions II and III of figure 1 is signalled by a decrease of the slope occurring at $T = 280$ K. We note that assuming a structural relaxation time τ_s of 100 s at T_g yields $\tau_s(280 \text{ K}) = 3 \times 10^{-7}$ s ($\tau_s \propto \eta$). The value is quite close to the longest ESR observation time (about 5×10^{-7} s). It is tempting to conclude that from the ESR standpoint below $T = 280$ K TEMPO reorientation takes place in a disordered *solid-like* OTP environment. The evidence of jump-like rotations and the Arrhenius temperature dependence of τ_2 (slope: $\Delta E = 18.7 \pm 1$ kJ mol $^{-1}$) are consistent with this view [11]. This picture suggests that in region II, where the FDSE law is observed, a change between a liquid-like (region I) and a solid-like (region III and IV) diffusion occurs.

The crossover from region III and IV of figure 1 occurs at $T = 238$ K, which is close to the calorimetric OTP glass transition ($T_g = 243$ K). In region IV the temperature dependence of τ_2 is described by an Arrhenius law with slope $\Delta E = 4.37 \pm 0.4$ kJ mol $^{-1}$.

In conclusion, we studied the reorientation of a nearly spherical probe molecule in the temperature range $200 \text{ K} < T < 370 \text{ K}$. Below $T = 308$ K the DSE law is not followed and the molecular rotations and viscosity decouple. In agreement with previous findings a DSE–FDSE crossover is found close to the critical temperature $T_c = 290$ K [8]. Further studies involving dissolving cylindrical paramagnetic tracers in OTP are in progress.

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