ESR evidence for two coexisting liquid phases in deeply supercooled bulk water

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Using Electron Spin Resonance spectroscopy (ESR), we measure the rotational mobility of probe molecules highly diluted in deeply supercooled bulk water and negligibly constrained by the possible ice fraction. The mobility increases above the putative glass transition temperature of water, \( T_g = 136 \) K, and smoothly connects to the thermodynamically stable region by traversing the so-called “no man’s land” (the range \( 150 - 235 \) K), where it is believed that the homogeneous nucleation of ice suppresses the liquid water. Two coexisting fractions of the probe molecules are evident. The two fractions exhibit different mobility and fragility, the slower one is thermally activated (low fragility) and is larger at low temperatures below a fragile-to-strong dynamic crossover at \( \sim 225 \) K. The reorientation of the probe molecules decouples from the viscosity below \( \sim 225 \) K. The translational diffusion of water exhibits a corresponding decoupling at the same temperature [Chen S-H, et al. (2006) The violation of the Stokes-Einstein relation in supercooled water. Proc. Natl. Acad. Sci. U.S.A. 103: 12974-12978]. The present findings are consistent with key issues concerning both the statics and the dynamics of supercooled water, namely the large structural fluctuations [Poole PH, Sciortino F, Essmann U, Stanley HE (1992) Phase behaviour of metastable water. Nature 360: 324-328] and the fragile-to-strong dynamic crossover at \( \sim 225 \) K [Ito K, Moynihan CT, Angell CA (1999) Thermodynamic determination of fragility in liquids and a fragile-to-strong liquid transition in water. Nature 398:492-494].

Abbreviations: DH, dynamical heterogeneity; DSE, Debye-Stokes-Einstein law; ESR, Electron Spin Resonance spectroscopy; FSC, fragile-to-strong dynamic crossover; LDL, high-density liquid; LDL, low-density liquid; SE, Stokes-Einstein law; NML, no man’s land; OTP, o-terphenyl; TEMPOL, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl

The physical properties of water are far from being completely understood. Several thermodynamic and dynamic anomalies are known or anticipated in the metastable supercooled regime which influence the equilibrium states and have deep impact in biology, astrophysics, glaciology and atmospheric science [1, 2, 3]. At ambient pressure the supercooled regime ranges between the commonly accepted value of the glass transition temperature \( T_g = 136 \) K and the freezing temperature \( T_m = 273.15 \) K. Above \( T_g \) amorphous water transforms into a highly viscous fluid [4, 5]. Crystallization into metastable cubic ice (I\(_h\)) at \( T_N \sim 150 \) K with further transformation to the usual hexagonal form of ice I\(_h\) is reported [1, 6]. On the other hand, bulk water at atmospheric pressure can be supercooled below its melting temperature down to the homogeneous nucleation temperature \( T_{IH} \sim 235 \) K below which it usually crystallizes to I\(_h\). Thus, the region between \( T_N \) and \( T_{IH} \) is often regarded as a region where liquid water cannot be observed (“no man’s land”, NML) [1]. Nonetheless, the coexistence of crystals and deeply supercooled liquids was suspected almost one century ago for bulk systems [7]. More recently, evidence that water and cubic ice coexist in thin films in the temperature range \( 140 - 210 \) K was reported [8, 9, 10, 11]. The existence of liquid water has been also shown experimentally in veins (or so-called triple junctions) of polycrystalline ice [12] which serve as interfacial reservoirs for impurities [13, 14, 15]. The size of such reservoirs is thermodynamically defined by surface forces, and also by the curvature of the surface (i.e., the Kelvin effect in veins) [11, 16]. In pure ice, the reservoir size increases when approaching the melting point [17].

This background motivated us to investigate the coexistence of ice and supercooled water in large volumes in an attempt to characterize the dynamical properties of the liquid, particularly in NML. Of major interest is the comparison with the results concerning the liquid behavior evidenced in small volumes, like nanoparticles [18, 19, 20] and nanometric films [4, 10], where homogeneous nucleation is bypassed.

NML is of paramount interest for a definitive picture of the supercooled water. Different scenarios predict their characteristic temperatures in NML, i.e., the singular temperature \( T_o \sim 225 \) K where most response functions appear to diverge [3], the fragile-to-strong dynamic crossover (FSC) temperature at \( T_{FSC} \sim 228 \) K [6, 21, 22], the strongly suspected second critical point at \( T_c \sim 220 \) K, \( P_c \sim 10^5 \) Pa [23] and the kinetic glass transition temperature \( T_{MCT} \sim 221 \) K [24, 25]. The existence of characteristic temperatures that viscous water close to \( T_o \) and normal water under equilibrium conditions are distinct, particularly due to the different static structural heterogeneities of the low-(LDL) and the high-density (HDL) states of water, the corresponding liquids of LDA and HDA amorphs [1, 2, 3, 19, 20, 26]. Viscous water is more structured and HDL-rich, whereas normal water is disordered and LDL-rich. This viewpoint is challenged by experimental results suggesting that supercooled water above \( T_o \) is an ultravisous fragile liquid smoothly connected to the equilibrium states above the melting temperature \( T_m \) [4]. As further example of the unusual properties of water in NML, the breakdown of the Stokes-Einstein law (SE), stating the constance of the quantity \( \kappa = Dn/T(T, D, n) \), being the temperature, the translational diffusion coefficient and the viscosity, respectively, has been evidenced at \( \sim 225 \) K by confining water in nanoparticles [18] and simulations [26, 27, 28]. That decoupling has been attributed to the occurrence of dynamical heterogeneity (DH), i.e., a spatial distribution of mobility, in structural glass formers and put into correspondence with the static structural heterogeneities of water [26].

Orientation and reorientation of water molecules deserve consideration. There is competition between orientational entropy and bond energy in water and the anomalies of the latter are thought to be closely related to the orientational order [26, 29]. The rotation of individual water molecules, mainly occurring by large jumps (\( \theta \sim 60^\circ \)) [30], changes constantly the connectivity of the H-bond network. Recent simulations [26, 27, 28] suggested that the SE breakdown in water

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must also be accompanied by the breakdown of the Debye-Stokes-Einstein law (DSE), accounting for the coupling between the viscosity and the rotational diffusion, as observed in experiments [31] and simulations [32] on molecular glassformers.

Outline of ESR spectroscopy

Electron Spin Resonance (ESR) spectroscopy detects the dynamics of the magnetization $M$ of an ensemble of electrons in the presence of a static magnetic field $B_0$ and under driving by (ideally) a rotating magnetic field $B_1(t) \perp B_0$ with angular frequency $\omega$ (typically $\omega/2\pi \sim 9\,\text{GHz}$) [33]. The electron has magnetic dipole moment $m$ which stems from its intrinsic angular moment (spin) $\hbar S$ with $\hbar = h/2\pi$, $\hbar$ being the Planck constant. For a free electron $m = -\gamma_e \beta_e S$ where $\gamma_e = 2.0023$ and $\beta_e$ are the electron Lande' g-factor and the Bohr magneton, respectively. If $B_1(t) = 0$ and the spins are isolated, $M$, if misaligned with respect to $B_0$, performs a precession around $B_0$ with angular Larmor frequency $\omega_0 = \gamma_e B_0$ where $\gamma = g_e \beta_e / \hbar$ is the magnetogyric ratio (Fig. 1a). The ESR spectroscopy usually investigates condensed-matter systems where the electron exchange energy with the surroundings. When the rotating field $B_1(t)$ is acted on the magnetization $M$, the latter undergoes a precession around $B_0$ with angular frequency $\omega$ in the stationary state (Fig. 1b). For $\omega \sim \omega_0$ a resonance is observed corresponding to a marked power absorption by the spin system.

Spin probes. Liquids are usually diamagnetic and therefore provide no ESR signal. The issue is circumvented by dissolving paramagnetic guest molecules (spin probes), usually nitroxide free radicals with one unpaired electron, at an extremely low concentration to make their influence on the host and their mutual interactions vanishingly small [33]. The unpaired electron is localized in a highly directional, i.e. anisotropic, molecular bond (see Fig. 2). On this basis, a quantum-mechanical analysis shows that the Larmor frequency of the dipole moment of the spin probe depends on the orientation of the latter with respect to $B_0$ (see Supporting Information (SI)).

Rigid-limit and motional narrowing of the lineshape. We now illustrate how the ESR lineshape conveys information on the rotational dynamics of the spin probe [33, 34, 35]. Additional details are found in SI. We first consider an ensemble of immobile spin probes, e.g. like in a frozen host, with different fixed orientations. The different resonances of their magnetic dipole moments are detected by sweeping the $\omega$ frequency of $B_1(t)$ and their superposition gives rise to a broad absorption with width $\Delta \omega_0$, usually referred to as rigid-limit or powder lineshape (Fig. 1c). If the spin probe undergoes a rotational motion, the Larmor frequency of the associated dipole changes randomly in time. Fig. 1d pictures the case of a reorientation occurring by sudden jumps separated by random waiting times with average value $\tau$ ($\tau$ denotes the rotational correlation time, i.e. the area below the normalized correlation function of the spherical harmonic $Y_{2,0}$ [34], see SI). The fluctuation gives rise to frequency averaging. In fact, let us consider two Larmor frequencies differing by $\delta \omega_0$. If the accumulated phase difference in a time $\tau$, $\delta \omega_0 \tau$, is less than one, the two frequencies cannot be distinguished and are replaced by their average. This process distorts the rigid-limit lineshape to an extent which is controlled by the product $\tau \Delta \omega_0$. Illustrative cases are shown in Fig. 1d. If $\Delta \omega_0 \gg 1$ the rigid-limit lineshape is rounded off on the frequency scale $1/\tau$. If $\Delta \omega_0 \sim 1$, the average process manifests as a coalescence of the lineshape (“motional narrowing”) which becomes extreme for $\tau \Delta \omega_0 \ll 1$. In the latter case the width of a single line is roughly given by $\Delta \omega_0^2 \tau$ [34].

Accessible range of the rotational dynamics. The longest detectable $\tau$ value of a nitroxide spin probe by ESR, $\tau_{\text{max}}$, is set by the changes of the Larmor frequency, occurring each $T_2^* \sim 0.1 \mu s$ on average, due to the magnetic field produced by the rotating methyl groups close to the unpaired electron [33]. If $\tau \gg \tau_{\text{max}} \equiv T_2^*$ the spin probe does not rotate within $T_2^*$ appreciably, the lineshape is independent of the reorientation rate $1/\tau$ and virtually coincident with the rigid-limit lineshape. On the other hand, in the extreme narrowing regime the line coalescence cannot lead to linewidth less than $\sim 1/T_2^*$ in that $T_2^*$ is the upper limit of the lifetime of the coherent oscillation of the magnetization [33]. Then, the shortest detectable $\tau$ value, $\tau_{\text{min}}$, is found when the linewidth $\Delta \omega_0^2 \tau_{\text{min}} \sim 1/T_2^*$. For nitroxide spin probes $\tau_{\text{min}} \sim 10 \mu s$.

Results and Discussion

Samples were prepared in a capillary (dia $\sim 100 \mu m$) by doping a small amount of triple distilled water with about 0.1% by weight of the polar spin probe TEMPOL, see Fig. 2. The ESR signal of TEMPOL is recorded during the slow reheating of the quenched sample. Details are given in Methods Section.

Influence of the crystallization. In occasional runs the crystallization occurring during the thermal cycle affects the ESR signal of the spin probes. The resulting artifacts are well known in aqueous solutions [13, 14, 36] and due to the possible strong confinement of the radicals in interstices between the ice grains with subsequent strong reduction of their mutual distance (see Methods). However, in most runs the signal is flawless. Henceforth, we focus on those cases where strong arguments lead to the conclusion that the ice loosely confines TEMPOL in liquid pockets.

Spin-probe mobility above 130 K. Fig. 2 presents the temperature-dependence of the ESR signal of the spin probe. As usual, the lineshape, due to phase-detection, is displayed in derivative mode by sweeping the static magnetic field $B_0$ with constant microwave frequency $\omega$. The lineshapes in Fig. 2 are strikingly similar to the usual ones of spin probes dissolved in viscous liquids [14, 31, 33, 36, 37, 38]. At low temperatures ($\leq 90^\circ\text{K}$) the ESR lineshape exhibits the rigid-limit pattern, namely the reorientation of TEMPOL is very slow (rotational correlation time $\tau \gtrsim \tau_{\text{max}} \sim 0.1 \mu s$). Above 120 K the ESR lineshape changes and its “motional narrowing” becomes apparent signaling the increased mobility of the spin probe. For $T \gtrsim 220^\circ\text{K}$ narrowing is extreme and the lineshape collapses to three lines. The three-lines pattern connects smoothly to the one detected in equilibrium condition at 300 K. Note that the observed narrowing of the lineshape is opposite to the crystallization-driven broadening discussed above.

The temperature dependence of the ESR lineshape shown in Fig. 2 excludes the possibility that the spin probes are trapped into the solid crystalline matrix developed during the initial quench-cooling or the subsequent slow re-heating (when the ESR data are collected). In fact, if trapping occurs during the quench, the rigid-limit ESR lineshape at 90 K should be observed on heating up to $T_m$, where a sudden collapse to a three-line pattern much similar to the one observed at 300 K should occur due to the large increase in mobility. Instead, one notes the continuous narrowing of the lineshape, i.e. the progressively increasing mobility of TEMPOL, across the supercooled region from, say, 120 K up to 300 K. Moreover, the motionally-narrowed lineshape at 220 K, pointing to fast reorientation, is almost identical to the one at 300 K indicating that TEMPOL has similar mobility at that temperatures. Since fast reorientation is also seen between 220 K and $T_m$ (see below), the trapping of the spin probes into the ice fraction can be safely ruled out. Instead, it has to be concluded that, when ice freezes, TEMPOL, as most impurities [13, 14, 15], is expelled from the ice and accumulate in liquid pockets [7, 8, 9, 10, 11, 12, 16, 17]. The volume

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fraction of the liquid water $\phi_w$ is estimated to be $\phi_w \gtrsim 0.04 - 0.07$ (see Methods).

**Dynamical heterogeneities.** In-depth numerical analysis of the ESR lineshape was first carried out by modeling the jump reorientation of TEMPOL in terms of the jump angle $\theta$ and the rotational correlation time $\tau$ (see Methods). When fitted to the experiment, the model, relying on a homogeneous mobility scenario, worked nicely except in the temperature region $140 - 180^\circ K$ and typical results are shown in Fig.2. In the temperature region $140 - 180^\circ K$ dynamical heterogeneity (DH) is apparent. In fact, entering the DH regime on heating, a second component, to be ascribed to a TEMPOL fraction with greater rotational mobility, appears (Fig.3). In the DH regime the lineshape was evaluated as a weighted sum of two components, i.e. the “fast” (F) component with weight $w_f$ and the “slow” (S) component with weight $w_s = 1 - w_f$. On increasing the temperature, $w_f$ increases and above $180^\circ K$, still well inside NML, $w_f \approx 1$ (see inset of Fig.4). The missing evidence of dynamical transitions above $180^\circ K$ is due to the limited ability of the ESR spectroscopy to discriminate between different TEMPOL rotational mobilities if the correlation times are too short ($\tau \lesssim 1\text{ ns}$) and cannot be taken as evidence of no actual DH.

**Temperature dependence of the spin-probe reorientation.** Fig.4 presents the temperature dependence of the model parameters describing the reorientation of the two TEMPOL fractions. It is seen that at the lowest temperatures the dominant S fraction of TEMPOL undergoes small-size diffusive rotational jumps with nearly constant $\tau_s$, correlation times. Crossing over $127^\circ K$, $\tau_s$ starts to drop and the jump size to increase which is consistent with a more mobile and open structure of the surroundings of TEMPOL consequent to the glass transition. At $140^\circ K$ the F component becomes apparent in the ESR lineshape and its weight increases with the temperature. The presence of the F fraction leads to no anomaly in the rotational dynamics of TEMPOL molecules belonging to the S fraction. In particular, $\theta$, levels off to $\approx 60^\circ$ (see Fig.4a) in agreement with simulations on water [30]. The DH regime ends at about $180^\circ K$ above which only the F component is seen. The correlation time $\tau_\gamma$ decreases with the temperature and shows an inflection point at about $225^\circ K$. At higher temperatures $\tau_\gamma$ connects smoothly to the equilibrium value at $300^\circ K$.

We note that the temperature dependence of the TEMPOL correlation times in Fig.4 shows a crossover at $225^\circ K$ from a high-temperature “fragile” behaviour (non-Arrhenius) to a lower-temperature “strong” one (Arrhenius) which strongly resembles the FSC crossover which has been hypothesized for water at $T_{\text{FSC}} \sim 225^\circ K$ [6] with recent support from simulation [21] and experiments in confined environments [22]. The observation of fragile behaviour in weakly supercooled water is fully consistent with the views that the water glass transition is kinetic in nature [24, 25].

**Breakdown of the Debye-Stokes-Einstein law.** Both the FSC and DH in supercooled water drive the breakdown of the SE and DSE relations [18, 26, 27, 28]. The DSE breakdown was already observed by ESR in supercooled liquids [31]. We evaluated the DSE ratio $R_{\text{DSE}} \equiv \eta/\tau(T)$ (to be constant according to the DSE law). To evaluate the water viscosity below $T_H \sim 235^\circ K$, we resorted to, after proper consideration (see Methods), a thermodynamic construction [39] based on the entropy-based Adam-Gibbs equation [40, 41]. Owing to the several thermodynamic constraints on the entropy of water, the construction provides tight bounds on $\eta(T)$ below $T_H$ provided that a maximum in the specific heat occurs at about $225^\circ K$ [39]. The latter has been recently observed [42]. Fig.5 shows the results about $R_{\text{DSE}}$ which are compared to the corresponding SE ratio $R_{\text{SE}}$ for nanocoated water [18]. At high temperatures both SE and DSE are weakly violated. In fact, the ratio $R_{\text{DSE}}$ increases by about 5.1 times from $280^\circ K$ down to $240^\circ K$ (the water viscosity increases by about 16 times [39]), whereas $R_{\text{SE}}$ increases by about 4.4 times for nanocoated water [18]. By decreasing the temperature below $\sim 225^\circ K$ one observes that both $R_{\text{DSE}}$ and $R_{\text{SE}}$ increase much more than at high temperature, i.e. the violations of both SE and DSE are much more apparent. So, we note that the SE as SE (see also Fig.3 of ref. [18]), undergoes a two-stage decoupling, i.e. a weak violation above $\sim 225^\circ K$ followed by a stronger decoupling at lower temperatures. The larger increase of $R_{\text{DSE}}$ with respect to $R_{\text{SE}}$ at lower temperatures is in agreement with simulations of water [27, 28] and molecular liquids (see [32] and ref.22 of that paper).

**Spin-probe sensing of the water static heterogeneities.** The correspondence between DH, the breakdown of SE and DSE and the presence of static heterogeneities in supercooled water, characterized by large fluctuations spanning a range of structures from HDL-like to LDL-like, has been explored with particular attention to the local orientational order [26, 27, 28]. It is interesting to put the evidence concerning the heterogenous dynamics of TEMPOL within this context. In the low-temperature region of the supercooled regime, the LDL fraction, characterized by better organization of the local tetrahedrally coordinated hydrogen-bonded network, is higher than the HDL fraction where the network is not fully developed [19, 20]. One expects that LDL exhibits slower rearrangements and lower fragility (i.e. more Arrhenius-like temperature dependence) than HDL. The temperature dependence $\phi(T)$ of the LDL fraction is larger at higher temperatures and connects smoothly to the equilibrium states above $T_m$ [19, 20]. This scenario suggests that TEMPOL senses the distribution of static structures of supercooled water. In particular, the S fraction senses LDL and the F fraction senses HDL. In fact, i) the S fraction of TEMPOL reorientates with Arrhenius behaviour, whereas the F fraction is more fragile, i.e. $\tau_s$ exhibits a non-Arrhenius temperature dependence (see Fig.4); ii) the weight of the F fraction increases with temperature and connects smoothly to the reorientation regime of TEMPOL above $T_m$.

ESR evidences LDL and HDL states of water in an indirect way via their influence on the spin-probe reorientation. This raises the question of their direct identification in the supercooled water-ice mixture. To do that, one needs a technique with good discrimination between the three distinct coexisting contributions, i.e. ice, LDL and HDL. From this respect, promising opportunities are offered by: i) the measurement of the vibrational spectra (HOH bending and OH-stretching modes) via Fourier transform infrared spectroscopy (see Fig.1b of ref. [19]) and ii) the measurement of the proton chemical shift $\delta_{\text{CH}_2}$ by NMR providing a picture of the intermolecular geometry (compare the data of Fig.1a of ref. [42] with $\delta_{\text{CH}_2} = 7.4\text{ppm}$ for a single crystal of hexagonal ice [43]).

In conclusion, ESR investigations of the rotational mobility of probe molecules dissolved in deeply supercooled bulk water provide evidence for two coexisting liquid phases between ~ 130 K and the thermodynamically stable region, including the ‘no man’s land’ (the range 150 – 235 K). Two distinct fractions of the probe molecules with different mobility and fragility are observed. It is argued that they sense the low- and the high-density states of supercooled water. The reorientation of the probe molecules exhibits fragile, i.e. non-Arrhenius, character at high temperature with a crossover to a strong behaviour below ~ 225 K. An analogous crossover has been hypothesized for water at $T_{\text{FSC}} \sim 225^\circ K$ [6]. The temperature dependence of the correlation time of the slow component shows a change in slope at ~ 127 K, close to the putative glass transition temperature of water at ~ 136 K. The reorientation of the probe molecules decouples from the viscosity below ~ 225 K (DSE breakdown), paralleling the behaviour of the translational diffusion of water [18].

**Materials and Methods**
Samples were prepared in a capillary (dia. ~ 100 µm) by doping a small amount of the distilled water with about 0.1% by weight of the polar radical TEMPOL (spin probe). TEMPOL accommodates well in water due to hydrogen-bonds and the moderate size ($r_{\text{TEMPOL}} \sim 0.34 \text{ nm}$ to be compared to
The ESR signal of TEMPOL are recorded by using a X-band Bruker ER 200 CW EPR spectrometer. Data are collected on heating the quenched samples. At a selected temperature no aging, i.e. no sample evolution, was ever detected.

The ESR lineshape provides information on the conditions of the sample during the experiment, particularly the degree of confinement of the spin probe between the ice grains and the amount of the interstitial liquid water above 1.30 K. In fact, the spin probes, as most impurities [13, 14, 15], are expelled from the ice close ones if the increased spin probe concentration, the magnetic field $B^{(v)}$ created by one spin probe is not negligible ($B^{(v)}/B$) ~ 150 Gauss at 0.5 nm [33]. Then, each spin probe sees an effective total magnetic field due to the surrounding ones $B_{\text{eff}} = B_0 + \sum B^{(v)}$. Due to the randomness of both the direction and the modulus of $B^{(v)}$, a distribution centered at $B_0$ and width about $B^{(v)}$ resulting in a very wide distribution of the Lamor frequencies $\omega_0 \propto |B^2|$, i.e. an apparent line broadening exceeding largely than the one observed under diluted conditions. In our experiments the line broadening due to the crystallization was observed only occasionally during the several experimental runs. This points to the conclusion that the crystallization does not yield a marked increase of the spin probe concentration in the liquid fraction of the water-ice mixture. The minimum liquid fraction $\phi_w$ of the sample which is needed not to observe crystallization effects on the ESR lineshape may be estimated. Let us assume that, due to the increased spin probe concentration, the magnetic field $B^{(v)}$ acted by one spin probe on the close ones is large enough to exceed any other broadening effect. At 220 K, the narrowest line of the observed triplet has width of about 1 – 2 Gauss (see Fig. 2). If the spin probes, with magnetic dipole equal to about the Bohr magneton $\mu_B$, have mutual average distance $d$, $B^{(v)} \propto \mu_B d^{-3}$ and $B^{(v)}$ ~ 1 – 2 Gauss if $d$ ~ 2.1 – 2.6 nm. If no ice is present, TEMPOL molecules are homogeneously dispersed in water with, given the adopted concentration, average distance $d$ ~ 0.4 nm. Then, $\phi_w \gtrsim (d/d_0)^3 \sim 0.04 – 0.07$.

The lineshape is evaluated by a stochastic memory-function approach (see Eq. 3.1) is given

$$\phi_w = \frac{\omega_0}{\omega_d}$$

where $\omega_0$ is the magnetic field due to the surrounding ones $B_{\text{eff}}$ and $\omega_d$ is the magnetic field due to the crystallization. The temperature-independent $\phi_w$ increases with the temperature $T$.

To get confidence on the thermodynamic extrapolation of the viscosity below $T_H \sim 235 K$ [39] we compared the DSE violation of TEMPOL in water with one of the spin probe TEMPO (virtually identical to TEMPOL) in the prototypical fragile glassformer o-terphenyl (OTP) [40]. This comparison shows that the magnitude of the DSE breakdown in water and OTP is quite similar and reassured us on the robustness of extrapolation.

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Fig. 1. Aspects of the ESR spectroscopy. a) Free precession of the magnetization $M$ of an ensemble of isolated electrons around the static magnetic field $B_0$ with Larmor angular frequency $\omega_0 = \gamma B_0$, $\gamma$ being the magnetogyric ratio. The transverse magnetization oscillates at the same frequency. b) In condensed matter, the electrons exchange energy with the surroundings. A rotating microwave field $B_1(t) \perp B_0$ with angular frequency $\omega$ forces the precession of the magnetization around $B_0$ with the same angular frequency. When $\omega \approx \omega_0$, an absorption resonance occurs. c) The magnetic dipoles $m$ of immobile spin probes in a frozen liquid have different $\omega_0$ values due to their different orientations with respect to $B_0$, thus resulting in a broad line with width $\Delta\omega_0$ (black line), usually referred to as rigid-limit or powder lineshape. d) If the spin probe undergoes rotation (sketched as instantaneous clockwise jumps at random times), $\omega_0$ fluctuates. When the rotational rate $1/\tau$ is larger than the width of the $\omega_0$ distribution $\Delta\omega_0$, the different precession frequencies become indistinguishable and an average value is seen, i.e., the ESR lineshape coalesces (motional narrowing).
Fig. 2. Selected ESR lineshapes of the spin probe TEMPOL in quenched bulk water and subsequent re-heating at the indicated temperature. Note that: i) for technical convenience the static magnetic field $B_0$, and not the microwave frequency $\omega$ as in Fig.1, is swept; ii) the phase-sensitive detection displays the lineshape in derivative mode. The chemical structures of TEMPOL (molecular size $r_{\text{TEMPOL}} \sim 0.34 \text{ nm}$) and water ($r_{\text{H}_2\text{O}} \sim 0.14 \text{ nm}$) molecules are sketched. The unpaired electron of TEMPOL (drawn as a dot) is localized in the NO bond. The theoretical predictions considering the reorientation of TEMPOL with (140K, 160K) and without dynamical heterogeneity are also shown.

Fig. 3. ESR lineshapes of TEMPOL in DH regime. Note the growth of the narrow component (fast TEMPOL) which superimposes to the broader one (slow TEMPOL) with increasing temperature. The insets show the fast (blue) and slow (green) components of the overall lineshape (red) at two temperatures.
Fig. 4. Temperature dependence of the rotational parameters of the fast (F) and the slow (S) fractions of TEMPOL in deeply supercooled bulk water. Main panel: rotational correlation times $\tau_S$ and $\tau_F$. Inset a: average jump angle of the S fraction. Inset b: weights of the F and S fractions. Note in the main panel: i) the knee at $\sim 127 \text{K}$ close to $T_g = 136 \text{K}$, ii) the DH regime ($140 - 180 \text{K}$) where the two coexisting TEMPOL fractions with different mobilities are evidenced, iii) the inflection close to $T_{FSC} \sim 228 \text{K}$.

Fig. 5. Breakdown of the DSE law. Data are compared with the SE breakdown from ref.[18]. Filled dots refer to temperatures where experimental values of the viscosity are available. Empty dots are based on a thermodynamic extrapolation of the viscosity [39]. The line across the dots is a guide for the eyes.