Quadrupolar Relaxation of $^{23}$Na$^+$ in Solution Beyond Rotational Models: Revealing a Link with Ultrafast Collective Dynamics by Experiments and Simulations

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The structure and dynamics of aqueous ions such as lithium, sodium, or potassium play a pivotal role in biology and in many industrial applications. Nuclear magnetic resonance (NMR) relaxometry represents a powerful tool for extracting dynamic information, but obtaining detailed links to molecular motion can be challenging. The relaxation for many of these ions is dominated by the quadrupolar interaction mediated by electric field gradient (EFG) fluctuations and its interpretation in terms of definite microscopic mechanisms is still lacking. Here we combine systematic quadrupolar relaxometry experiments with ab initio calculations and classical molecular dynamics simulations to account for both the electron cloud contribution to the quadrupolar coupling constant and long-time EFG fluctuations. For aqueous sodium ions, we show that this approach yields a good agreement between the calculated and experimentally measured NMR rates both in dilute and concentrated electrolyte solutions over a broad range of temperatures. For increasing salt concentration or decreasing temperature, we find that the growth of the quadrupolar NMR relaxation rate is mainly due to the slowing down of EFG fluctuations. The quadrupolar coupling constant is marginally affected by concurrent modifications of the ion’s solvation shell structure, yet it counterintuitively increases with temperature. We further demonstrate that the commonly-assumed rotational models fail to account for the measured effects and significantly overestimate the correlation times. In contrast, we find that the EFG relaxation occurs over a time scale compatible with that of the structural relaxation of the solution that we determine from stress correlation functions. We therefore conclude that quadrupolar NMR relaxometry of $^{23}$Na$^+$ can sense the fast collective dynamics around the solute that drive the electrolyte structural rearrangements within the THz domain. These findings pave the way for the development of mesoscopic models that could be relevant in biological systems to characterize e.g. ion dynamics in tissues using sodium NMR relaxation or imaging.

I. INTRODUCTION

The proper characterization and modeling of the solvation structure of alkaline cations (e.g., Li$^+$, Na$^+$, and K$^+$) in aqueous solution is of considerable interest both in the studies of physiologically relevant systems as well as in the potential investigation of electrolytes within the context of electrochemical devices. Nuclear magnetic resonance (NMR) spectroscopy has been an excellent source of dynamic and structural information for a number of nuclear species, including $^{23}$Na that has a nuclear spin $3/2$ with close to 100% natural abundance, and produces the second strongest NMR signal after protons in biological tissues. Concurrent measurements of both the $^1$H and $^{23}$Na nuclei can provide a method for absolute thermometry in magnetic resonance imaging. The NMR sensitivity of sodium is 9.2% of that of proton, while the typical concentration can be three, or more, orders of magnitude lower than the proton concentration. As a consequence, in biological systems the sodium signal-to-noise ratio is 3,000–12,000 times lower than that of $^1$H. Nonetheless, the longitudinal relaxation time $T_1$ of $^{23}$Na (typically 40 ms and below) is short compared to that of $^1$H (on the order of seconds), allowing for rapid averaging of the signals such that quantitative analysis is made possible within reasonable time scales.

The shortness of the $^{23}$Na NMR relaxation times is due to a fluctuating quadrupole interaction related to the changes in the hydration sphere and the proximity of other ions. The relaxation rate is determined from a combination of the strength of the electric field gradient (EFG) around the ion, quantified by means of the quadrupolar coupling constant (QCC) $C_Q$ and the characteristic correlation time $\tau_c$ with which the memory of...
fluctuations is lost. While absolute values of $\tau_c$ can provide fundamental insights into the molecular mechanisms behind the quadrupolar relaxation and can be potentially correlated with useful dynamic properties, such as diffusion coefficients, solution viscosity, and conductivity \cite{16, 18}, their unambiguous determination from the experimentally measured rates has remained essentially impossible due to the limited knowledge on the QCC of $^{23}$Na in aqueous electrolytes that is sensitive to the local ionic hydration shell structure \cite{19, 20}. In principle, the correlation time can be extracted independently from the maximum of $1/T_c$ that develops with reducing the system temperature \cite{21, 24}. Yet, as most aqueous electrolyte solutions freeze close to 0 °C, that approach was almost entirely restricted to the NMR relaxation of $^7$Li in certain concentrated lithium halides that can be supercooled down to around -100 °C \cite{24}. Despite the fact that $\tau_c$ of $^7$Li was found to be close to that of $^1$H in water molecules, suggesting that the reorientation water dynamics is at play in the quadrupolar relaxation mechanism \cite{29}, the peculiar experimental conditions with highly concentrated and supercooled solutions as well as the reliance on the single-exponential relaxation model for both $^7$Li and $^1$H to interpret the data shed doubt on the universal applicability of the latter conclusion.

Different models have been suggested to rationalize the quadrupolar relaxation both in terms of dielectric theories, mode-coupling analysis, and definite molecular processes. Hynes and Wolynes developed an analytical theory based on the quadrupole reorientation dynamics in a continuous dielectric solvent \cite{25}. Perng and Ladanyi dropped the continuous solvent description in their refined dielectric theory that coupled the field gradient dynamics to solvent charge density fluctuations \cite{26}. While the continuous dielectric theory of Hynes and Wolynes \cite{26} typically underestimated the predicted values of the quadrupolar rates, the theory of Perng and Ladanyi \cite{20} was able to achieve quantitative agreement with experiments, yet it relied on a free parameter. Bosse et al. formulated a mode-coupling theory for the EFG relaxation in molten salts \cite{27}. A series of models of Hertz et al. related the correlation time of EFG fluctuations to water dipole reorientation \cite{28, 30}. However, this molecular mechanism was shown to significantly oversimplify many-body correlations in the context of quadrupolar relaxation dynamics \cite{31, 33}. More recently, the EFG correlation time was suggested to be interpreted as the rotational correlation time for an object in a continuous solvent \cite{16, 18}, likely to be associated with collective stochastic rotations of the ionic solvation shell \cite{31, 33}. While rotational diffusion is clearly at play in the case of intramolecular quadrupolar relaxation \cite{36}, as for the relaxation of $^2$H in heavy water, its applicability to the problem of single quadrupolar ions that is inherently intermolecular is debatable and requires a thorough investigation.

Both ab initio \cite{37, 41} and classical \cite{20, 32, 33, 42} molecular dynamics (MD) simulations have become indispensable tools in assessing predictions of the above-mentioned theories. In particular, the isotropic monoeXponential character of the quadrupolar relaxation dynamics that is often assumed in theories with a continuous solvent description was challenged both at the ab initio and classical levels. Using classical MD, Roberts and Schnitker \cite{32} highlighted a pronounced effect of intermolecular cross correlations on the EFG relaxation that are treated in a rather simplified fashion within molecular models \cite{28, 30}. Carof et al. \cite{39} underlined a major role of collective fluctuations in ionic solvation shells on the EFG dynamics. Compared to classical MD approaches that rely on approximations for the electron cloud contribution to the EFG at the ion position \cite{20, 45, 48, 49}, ab initio methods provide the best accuracy of the computed QCC \cite{37, 39, 50, 52}. However, the associated high computational cost often impedes the long-time sampling of EFG fluctuations \cite{37, 38} and, hence, the accuracy of the correlation time estimates, even in the case of infinitely diluted aqueous ions \cite{37, 39}. Therefore, the use of the fully first-principles approach may not be appropriate in concentrated electrolyte solutions considered here, for which the quadrupolar NMR relaxation slows down with increasing salt concentration and decreasing temperature \cite{28, 30, 44}.

In this work, we find that $C_Q$ calculated at the ab initio level in conjunction with $\tau_c$ evaluated classically allows reaching good agreement with the experimentally obtained quadrupolar rates for the $^{23}$Na$^+$ relaxation in aqueous electrolyte solutions at different salt concentrations and temperatures. We utilize the microscopic information available in MD to show that the main effect of increased relaxivity is due to a lengthening of the correlation times of the electric field gradient fluctuations, rather than a change of the average quadrupolar coupling constant, that we determined for $^{23}$Na$^+$ in several electrolyte solutions. We demonstrate that the relaxation of EFG fluctuations features a consistent two-step structure with a rapid initial decay, whose time scale is similar to that of librational water dynamics, followed by a much slower non-exponential relaxation at longer times. We find that the second non-exponential decay primarily affects the lengthening of the correlation time with increasing salt concentration or decreasing temperature, thereby suggesting a collective origin of the observed behavior. Combining experimental and simulations results, we then discuss $\tau_c$ in relation to a rotational diffusion process. We show that the time scale estimated both from the Stokes-Einstein Debye relation and from the water dipole reorientation (the latter arising in Hertz models), overestimate the correlation time of EFG fluctuations by at least an order of magnitude. Contrary to the commonly-assumed picture, we conclude that the rotational motions do not constitute the prevailing pathways behind the quadrupolar relaxation. Rather, we find that $\tau_c$ is strongly correlated with and similar to the characteristic time scale of the electrolyte’s structural relaxation that we obtain from the stress relaxation dynamics in
our molecular simulations. Therefore, our results suggest that the short-time collective dynamics of the liquid primarily drive the quadrupolar relaxation at the position of sodium ions.

II. METHODS

A. Theory

The quadrupolar mechanism dominates the relaxation of nuclei with spin $I > 1/2$ and is due to the coupling between their quadrupolar moment $eQ$ with the EFG tensor $V$ at the nucleus position $r$. While the NMR relaxation of spin components is generally bi-exponential in the case of $^{23}$Na with $I = 3/2$ [24, 53], it is possible to define effective longitudinal and transverse quadrupolar relaxation rates in more detail in the Supplemental Material (SM), in the fast motion regime, the two quadrupolar relaxation rates become equal and, combined with the rotational invariance of the system, can be expressed as [32]

$$\frac{1}{T_1} = \frac{2I + 3}{20I^2(2I - 1)} \left( \frac{eQ}{\hbar} \right)^2 \int_0^\infty dt \langle V(0):V(t) \rangle,$$

(1)

where $\langle V(0):V(t) \rangle = \sum_{\alpha,\beta} (V_{\alpha\beta}(0)V_{\alpha\beta}(t))$ with $\alpha, \beta = x, y, z$, the brackets $\langle \rangle$ denote an ensemble average, and $\hbar$ is the reduced Planck constant. The relation (1) enables a microscopic definition of an effective correlation time of the EFG fluctuations $\tau_c$

$$\tau_c = \langle V^2 \rangle^{-1} \int_0^\infty dt \langle V(0):V(t) \rangle,$$

(2)

and allows us to formally separate static and dynamic contributions to the integral of the EFG autocorrelation function (ACF) $\langle V(0):V(t) \rangle$ that are given by the variance $\langle V^2 \rangle = \langle V(0):V(0) \rangle$ and $\tau_c$, respectively. Specifically for a $^{23}$Na nucleus with $I = 3/2$ and $Q = 104 \times 10^{-31}$ m$^2$ [56], the rate constant $1/T_1$ becomes

$$\frac{1}{T_1} = \frac{C_Q^2 \tau_c}{10},$$

(3)

with the QCC defined via $C_Q^2 = \frac{2}{3} \left( \frac{eQ}{\hbar} \right)^2 \langle V^2 \rangle$ [36, 37] (see also Supplemental Sec. 1A). In what follows, $C_Q$ and $\langle V^2 \rangle$ will be used interchangeably to rationalize the EFG strength at the position of $^{23}$Na$^+$ ions.

Eq. (1), which follows from linear response theory, allows to straightforwardly calculate the quadrupolar spin-lattice relaxation rate $1/T_1$ from the EFG fluctuations in equilibrium MD simulations without an imposed magnetic field. Nevertheless, the accuracy of the ACF integral in Eq. (1) is often limited by the fact that both reliable values of the EFG at the nucleus that include the electron cloud contribution and a sufficiently long sampling of its fluctuations are necessary. Accurate EFGs can be obtained with electronic structure calculations based on the density functional theory (DFT) [51] that make use of the pseudopotential-based projector-augmented wave (PAW) approach to reconstruct the all-electron charge density in the region close to the nucleus [37, 38, 50, 52] or cluster calculations with all-electron orbitals [37, 40, 41]. Such DFT-based EFG calculations are often combined with ab initio molecular dynamics to generate system configurations [37, 41]. Yet, as mentioned above, the high computational cost of ab initio methods frequently hinders the resulting accuracy of the correlation time estimates in Eq. (2) [37, 39].

Here, we rely instead on a semi-classical approach that draws upon the electrostatic picture of the intermolecular EFG relaxation, according to which the electron cloud polarization arises mainly from the external charge distribution around a given monoatomic ion [28, 29, 57]. Note that the latter assumption discards the electron density polarization that originates from non-electrostatic effects, such as short-range repulsion [19, 58, 59], that might be necessary to reach quantitative agreement with the experiments. In the simplest case, the full EFG at the nucleus position, $\mathbf{V}$, is considered to be proportional to the EFG generated by the external charges, $\mathbf{V}_{\text{ext}}$, constituting the so-called Sternheimer approximation [48, 49]:

$$\mathbf{V} \simeq (1 + \gamma)\mathbf{V}_{\text{ext}},$$

(4)

where $\gamma$ is the Sternheimer (anti)shielding factor that is typically large $\gamma \gg 1$. The widely-used approximation (4) permits to calculate the quadrupolar spin-lattice relaxation rate (1) using the stochastic dynamics of $\mathbf{V}_{\text{ext}}$ from classical MD [32, 42, 43, 47] to facilitate the long-time sampling of EFG fluctuations. Yet, a consistent value of $\gamma$ that reflects the charge density representation in a given classical force field (FF) at hand (that is, specific partial water point charges and induced dipoles) needs to be derived using auxiliary ab initio calculations [20]. Despite the straightforward nature of the Sternheimer approximation, in Sec. III A we will demonstrate that the relation (4) in fact systematically underestimates the EFG variance even with consistently derived $\gamma$-factors over a broad range of salt concentrations. In contrast, $\langle V^2 \rangle$ obtained with DFT PAW calculations combined with $\tau_c$ sampled in classical MD allows us to reach good agreement between the simulations and experiments.
B. Molecular dynamics simulations

Aqueous sodium chloride (NaCl), bromide (NaBr), and fluoride (NaF) solutions were simulated using classical MD employing the Madrid-2019 FF [60] that is based on the TIP4P/2005 water model [61] and uses scaled charges of +0.85e and -0.85e (e is the fundamental unit of charge) for Na\(^+\) cations and Cl\(^-\), Br\(^-\), and F\(^-\) anions, respectively. The scaled ionic charges aim at taking into account the electronic contribution to the dielectric constant at high frequencies in a mean-field fashion [62]. At a moderate computational cost in comparison to fully polarizable models, the EFG relaxation within the Madrid-2019 FF [60] has recently been shown to accurately describe the quadrupolar NMR relaxation rates of alkali metal ions at infinite dilution [20], in particular that of Na\(^+\). Solutions comprised of \(N = 1000\) water molecules and \(N_p\) ion pairs were initialized at different salt concentrations \(c\) in molal (denoted with mol·kg\(^{-1}\) or m) between \(0.06\) m \((N_p = 1)\) and \(4\) m \((N_p = 72)\) in a cubic box at the equilibrium solution density \(\rho(c, T)\) obtained in \(NPT\) simulations at \(P = 1\) bar. The densities are in excellent agreement with the experimental ones, as discussed in Supplemental Sec. 1B and shown in Supplemental Fig. S1.

The equilibrated electrolyte systems were then simulated in the \(NVT\) ensemble. Both \(NPT\) and \(NVT\) simulation runs were carried out in the open-source MetalWalls package on graphics processing units [63] with electrostatic interactions computed with Ewald summation [64] and a short-range cutoff of 1.24 nm. The constant temperature was maintained using the Nose-Hoover chains thermostat with a time constant of 1 ps. System temperatures in range from 10 °C to 50 °C were considered. The equations of motion were integrated using the velocity Verlet algorithm and an integration time step of 1 fs. The effective rigidity of water molecules was imposed with the help of the RATTLE algorithm with a precision of \(10^{-9}\). For each \((c, T)\) state point, at least five independent runs of length 5 ns were performed to measure the EFG at the ion positions (sampled every 50 fs). Full Ewald summation expressions [64] were used in the computation of the EFGs, as recently implemented in MetalWalls [20]. For the considered system parameters, the relaxation of EFG fluctuations was found not to be affected by the finite box size, as we show in the Supplemental Fig. 2. Finally, due to qualitative similarity of the EFG relaxation of \(^{23}\)Na\(^+\) in different electrolyte solutions considered here, in what follows we will focus on the case of aqueous NaCl, whereas the results pertaining to NaBr and NaF are discussed in Supplemental Sec. II.

C. Ab initio calculations

To determine EFGs with the electron cloud contribution, smaller systems containing 55 water molecules and \(N_p = 1, 2, 3, 4,\) and 5 NaCl ions pairs, corresponding to the salt concentrations \(c = 1, 2, 3, 4, 5\) mol·kg\(^{-1}\), were simulated in the same way as the larger ones described in Sec. II B. In a single \(NVT\) simulation run at \(T = 25\) °C, 2000 configurations were sampled with a period of 10 ps, and were later used in DFT-based EFG calculations with periodic boundary conditions in the Quantum Espresso (QE) package [65]. No additional geometry optimization of the configurations was performed in the DFT calculations. The PAW method [60, 52, 66] was used to reconstruct the all-electron charge density in the vicinity of the nucleus using the QE-GIPAW package [67]. The self-consistent electron densities were calculated using the PBE functional [68], a kinetic energy cutoff of 80 Ry, and norm-conserving pseudopotentials of the GIPAW package [69]. In the case of Na\(^+\) ions, the EFGs obtained with the PBE functional were shown to be in good agreement [39] with those obtained with the hybrid PBE0 functional [70]. A representative system configuration of a NaCl solution at 5 mol·kg\(^{-1}\) highlighting the converged charge densities is shown in Fig. 1(a).

D. NMR experiments

Solution samples with 9 different NaCl concentrations were prepared by mixing \(x\) mg of NaCl in \((y-x)\) mg of deionized water in a beaker, with \(x = 0.1, 0.2, 0.5, 0.8, 1.1, 1.4, 1.7, 2.0, 2.3\) mg and \(y = 10\) mg, to make solutions of concentrations \(0.173, 0.349, 0.901, 1.488, 2.115, 2.786, 3.505, 4.278,\) and \(5.111\) mol·kg\(^{-1}\) to 5 mm NMR tubes (sample volume = 0.5 mL). All mass measurements were performed on a Mettler Toledo ME204E balance with a resolution of 0.1 mg. The solution at 26% weight corresponds to NaCl saturation in water at 20 °C [71].

NMR experiments were performed on an 11.7 T NMR Bruker Avance I spectrometer operating at 132.3 MHz for \(^{23}\)Na, using a 5 mm double resonance broadband probe. The test tubes with the solutions were placed inside the spectrometer where the sample temperature could be controlled using gas flow and a temperature sensor providing a precise, stable and reliable temperature regulation. After each desired temperature reached steady state, a standard free induction decay was acquired followed by a longitudinal relaxation time \(T_1\) mapping sequence, and a diffusion pulse sequence. At each temperature, the tuning and matching was checked. The duration of the 90° pulse was 9.6 μs, whereas that for the 180° pulse was 19.6 μs. A standard inversion-recovery pulse sequence was used to acquire \(T_1\) with 32 logarithmically spaced steps. The delay was varied from 1 ms to 400 ms for \(^{21}\)Na. Diffusion coefficients were measured using a Pulsed-Gradient-Spin-Echo in 32 steps with a maximum \(b\)-value of 2200 s·mm\(^{-2}\). The maximum diffusion gradient was 1 T·m\(^{-1}\) and the duration was 4 ms.
These changes of the Sternheimer factor for Na$^+$ are consistent with previous findings that it is possible to define effective Sternheimer factors \( \gamma_{\text{eff}} \) for Na$^+$ as a function of salt concentration \( c \) (yellow squares). In addition, we show configuration-resolved \( \gamma_{\text{eff}} \) for Na$^+$ forming contact ion pairs (CIP, green triangles), solvent-shared ion pairs (SSIP, red diamonds), and solvent-separated ion pairs (SSIP, violet pentagons) with the Cl$^-$ anion. The alternative effective Sternheimer factor \( \gamma_{\text{eff}} \) obtained as \( (1 + \gamma_{\text{eff}})^2 = (V_{\text{AI}})/V^\alpha_{\beta} \) for different salt concentrations \( c \) (blue circles). (d), The variance of the EFG at the Na$^+$ positions for different \( c \) as obtained directly with ab initio calculations (green triangles), or using the value of \( \gamma_{\text{eff}} \) (yellow squares) and \( \gamma'_{\text{eff}} \) (blue circles) at infinite dilution. The error bars in (c) and (d) were calculated with bootstrapping.

III. RESULTS AND DISCUSSION

A. Modeling the electron cloud contribution to the electric field gradient

As the accuracy of the computed quadrupolar NMR relaxation rates in Eq. (1) profoundly depends on the electron cloud contribution to the EFG at the ion position [20] [39] [45], in this section we will assess different parametrization strategies for its inclusion. As already noted in Sec. I in the simplest case of the Sternheimer approximation [4], it is assumed that the full EFG at the nucleus is proportional to the EFG created by the external charge distribution, \( V \simeq (1 + \gamma)V_{\text{ext}} \), where the effect of the electron cloud polarization is incorporated via the rescaling factor \( 1 + \gamma \). Using a set of electrolyte configurations generated with classical MD, the validity of such approximation can be tested by comparing \( V_{\text{ext}} \) arising from the FF-based charge distribution against the full EFG \( V \) evaluated by means of ab initio calculations [20] [45]. If a correlation between these two quantities exists, it is possible to define an effective Sternheimer factor \( \gamma_{\text{eff}} \) [45], whose value depends in general on the classical FF at hand [20].

While the Sternheimer relation [4] has been explicitly validated for aqueous ions at infinite dilution [20] [45], the possibility of its application at high salt concentrations, where the ionic solvation shell structure changes [72] (see also Supplemental Section II B), remains unexplored. To systematically address this question, we have compared ab initio, \( V_{\text{AI}} \), and classical, \( V_{\text{ext}} \), EFGs at the position of Na$^+$ ions computed on the same set of solution configurations, as detailed in Sec. II C. Similarly to the infinite dilution case [20], we find a strong correlation between the components of \( V_{\text{AI}} \) and \( V_{\text{ext}} \) for all concentrations considered here (up to \( 5 \) mol·kg$^{-1}$), as seen in Fig. 1(b) for the two extreme cases. Such a correlation allows us to define effective Sternheimer factors \( \gamma_{\text{eff}} \) through the linear fit \( V_{\text{AI}} = (1 + \gamma_{\text{eff}})V_{\text{ext}} \). The resulting \( \gamma_{\text{eff}} \), shown with yellow squares in Fig. 1(c), feature a very small increase with the salt concentration \( c \) (up to 2% compared to the infinite dilution case) and are sensitive to the sodium’s solvation state. In particular, the ensemble-averaged values of the Sternheimer factor \( \gamma_{\text{eff}} \) are consistent with those calculated from a subset of configurations forming solvent-shared NaCl ion pairs (SSIP), highlighted with red diamonds in Fig. 1(c). The SIP, which we define as the cation-anion pair located at the distance 3.39 Å < \( r_{\text{Na}-\text{Cl}} \) < 5.57 Å with the boundaries given by the first two minima of the Na-Cl radial distribution function (see Supplemental Figs. S3-S5), constitutes the most probable solvation state of Na$^+$ cations for \( c > 1 \) mol·kg$^{-1}$ (Supplemental Fig. S3). The values of Sternheimer factors obtained on a subset of contact ion pairs (CIP), for which \( r_{\text{Na}-\text{Cl}} < 3.39 \) Å, are somewhat enhanced in comparison to the ensemble average (green triangles in Fig. 1(c)), whereas the ones found for solvent-separated ion pairs (SSIP), for which we consider \( r_{\text{Na}-\text{Cl}} > 7.9 \) Å, are consistent with the infinite dilution value of \( \gamma_{\text{eff}} \) (violet pentagons in Fig. 1(c)). Finally, note that the solvation state dependent Sternheimer factors reported in Fig. 1(c) were extracted from a set of at least 50 independent hydration shell configurations of Na$^+$ ions.

The small changes of the Sternheimer factor for Na$^+$ in different ionic solvation states as well as with increasing the salt concentration indicate that its value obtained at
infinite dilution, $\gamma_{\mathrm{eff},0} = 10.54 \pm 0.11$ [20], should provide a reasonable approximation for determining the variance of the full EFG used in the calculation of the quadrupolar NMR rate in Eq. (3). The associated relative changes of $\gamma_{\mathrm{eff}}$ is less than 5% with respect to the value of $\gamma_{\mathrm{eff},0}$. Nevertheless, the variances of the EFG predicted within the Sternheimer approximation, $(1 + \gamma_{\mathrm{eff},0})^2 \langle V_{\mathrm{ext}}^2 \rangle$, underestimate the variance of the ab initio EFG, $\langle V_{\mathrm{AI}}^2 \rangle$, by more than 20% (compare yellow squares to green triangles in Fig. 1(a)). This again underlines the deficiencies of the simplistic Sternheimer approximation [20] that does not take into account non-electrostatic electron cloud polarization effects [19]. While the inclusion of higher order terms that depend on the external electric field at the position of an ion was suggested as a non-linear extension to the simple Sternheimer approximation [58, 73], it has not led to noticeable improvement in the predicted EFG variance for single aequous ions [20], again highlighting the importance of the electron density polarization due to short-range repulsion [19].

To improve upon the accuracy of the calculated quadrupolar coupling constants, the EFG variance $\langle V^2 \rangle$ can be evaluated directly from quantum DFT for each state point $(c, T)$ of interest, as explained in Sec. IIC. Formally, the use of ab initio EFG variances can be achieved by defining the Sternheimer factor $\gamma_{\mathrm{eff}}$ as

\begin{equation}
(1 + \gamma_{\mathrm{eff}}')^2 = \frac{\langle V_{\mathrm{AI}}^2 \rangle}{\langle V_{\mathrm{ext}}^2 \rangle}
\end{equation}

that incorporates the state-dependent variances $\langle V_{\mathrm{AI}}^2 \rangle$ and $\langle V_{\mathrm{ext}}^2 \rangle$. The values of $\gamma_{\mathrm{eff}}'$ obtained for increasing the salt concentration at $T = 25 ^\circ \mathrm{C}$ are shown with blue circles in Fig. 1(c). Similarly to the behavior of $\gamma_{\mathrm{eff}}$, $\gamma_{\mathrm{eff}}'$ slowly grows with $c$ within the considered range of concentrations, yet starting from a markedly enhanced value of $\gamma_{\mathrm{eff},0}' = 12.09 \pm 0.14$ at infinite dilution. The relatively small increase of $\gamma_{\mathrm{eff},0}'$ with the concentration indicates that $(1 + \gamma_{\mathrm{eff},0}')^2 \langle V_{\mathrm{ext}}^2 \rangle$ can provide a reasonable approximation for $\langle V_{\mathrm{AI}}^2 \rangle$. Indeed, as seen in Fig. 1(d), within the considered range of concentrations it yields values of the EFG variance that are within 5% accuracy of $\langle V_{\mathrm{AI}}^2 \rangle$, a much better estimate in comparison to the simple Sternheimer approximation [4]. Note that the latter translates into a possible 5% error of the computed NMR rates in Eq. (3), as $1/T_2$ is directly proportional to $\langle V^2 \rangle$. More importantly, such approximation permits the parametrization of the EFG variance from the ab initio calculations for ions at infinite dilution and allows to avoid computationally expensive DFT calculations at multiple system state points of interest. In summary, while not capturing all condensed-phase effects that arise with increasing $c$, $(1 + \gamma_{\mathrm{eff},0}')^2 \langle V_{\mathrm{ext}}^2 \rangle$ provides a fair accuracy and reproduces the trend of $\langle V_{\mathrm{AI}}^2 \rangle$ to decrease with the salt concentration (see Fig. 1(d)). As we show in what follows, the latter approach provides a good description of the quadrupolar NMR rates of $^{23}\text{Na}$ in combination with $\tau_c$ obtained from the dynamics of the EFG at the classical level.

B. Relaxation of electric field gradient fluctuations

While most of the previous studies focused on the quadrupolar NMR relaxation of ions at infinite dilution, as considered both at the classical [20, 32, 33, 42–46, 74] and ab initio [37, 39–41] levels, here we investigate the mechanisms behind the concentration and temperature behavior of the NMR rates [24, 28, 29]. To capture dynamic fluctuations that drive the quadrupolar NMR relaxation, the EFG at the ion positions was computed at the classical level from the point charges of water molecules and ions in the Madrid-2019 FF [60] (see Sec. II B). Two facts give confidence in this approach: (i) there exists a very strong correlation between the full and classical (external) EFGs (Fig. 1(b)), indicating that the dynamics of the former should be largely determined by that of the latter; (ii) while classical MD with rigid water molecules do not quantitatively reproduce the librational water dynamics or hydrogen-bond stretching that occur at very short times scales below $\sim 50$ fs [75], it is expected that these high frequency motions do not significantly affect the dominating long-time ($\sim 1$ ps) EFG relaxation mode (e.g., see Ref. [46] and the discussion further below).

Figs. 2(a) and 2(b) show the ACFs of the EFG at the Na$^+$ position, $C_{\mathrm{EFG}}(t) \equiv \langle V_{\mathrm{ext}}(0) V_{\mathrm{ext}}(t) \rangle$, as a function of salt concentration $c$ at $T = 25 ^\circ \mathrm{C}$ and of temperature $T$ at $c = 1$ m, respectively (ACFs at other system parameters are shown in Supplemental Fig. S6). The EFG fluctuations were sampled for over 25 ns, permitting us to obtain an accurate decay of the ACF for more than two decades starting from the initial value $C_{\mathrm{EFG}}(0)$. Similarly to a single Na$^+$ in water [20, 32, 39, 45], the decay of $C_{\mathrm{EFG}}(t)$ occurs in two steps: (i) a rapid initial decay happening at $t \lesssim 0.2$ ps that corresponds to $\approx 70\%$ of the EFG decorrelation. The latter finding is in good agreement with the initial decay of the EFG ACF as obtained with ab initio methods for Na$^+$ at infinite dilution [39], highlighting the validity of the classical approach; (ii) a much slower secondary decay occurring at the picosecond time scale. Evidently, as seen in Figs. 2(a)-(b) and also discussed in Supplemental Sec. II E for other electrolyte solutions, the increase in $c$ and the decrease in $T$ leave the initial fast decay practically unchanged, while causing a pronounced slow-down of the second decay mode. The latter is again highlighted in Fig. 2(c) that shows the EFG ACFs for $t < 1$ ps for different values of $c$ at $T = 25 ^\circ \mathrm{C}$ (see also Supplemental Fig. S7).

The decay of the EFG ACFs in Fig. 2 points out that the concentration and temperature dependence of the relaxation is primarily driven by collective dynamics in the ionic solvation shell. After the initial fast decay that can be described with an exponential $\sim e^{-t/\tau_c}$ with a time constant $\tau_c \approx 62$ fs for all $c$ and $T$, we find a development of a much slower relaxation mode that profoundly depends on the system parameters $c$ and $T$. In comparison to earlier results [46], our long-time sampling reveals that the slow decay of the EFG ACF is not monoexponential,
FIG. 2. Relaxation of EFG fluctuations. Normalized autocorrelation functions $C_{EFG}(t)/C_{EFG}(0)$ of the EFG at the position of a Na$^+$ ion obtained using classical MD simulations (a) for different salt concentrations at $T = 25^\circ$C and (b) for different temperatures at $c = 1$ m in aqueous NaCl solutions. Qualitatively similar trends are found for other concentrations and temperatures (see Supplemental Sec. II C). Shaded regions in (a) and (b) indicate standard errors from multiple independent simulation runs. (c), Short-time behavior of $C_{EFG}(t)$ for $t < 1$ ps at $T = 25^\circ$C for different concentrations. (d), Long-time behavior of $C_{EFG}(t)$ plotted on a double logarithmic scale at $c = 4$ m for different temperatures (the legend shown in (e)). The black solid and dashed lines highlight a power-law scaling $\sim t^\alpha$ with $\alpha = -5/2$ and $\alpha = -3/2$, respectively. (e), Same as in (d) but with $C_{EFG}(t)$ multiplied by $t^{5/2}$. The black dashed lines in (a), (b), (d), and (e) indicate stretched exponential fits with $\beta = 0.67$.

as clearly seen from the behavior of $C_{EFG}(t)$ on a semi-logarithmic scale in Figs. 2(a)-(b) and as we show with explicit fits in Supplemental Sec. II C. While the slow process can be well approximated with a single exponential for $t <\approx 2$ ps for most values of $c$ and $T$ considered here (Supplemental Fig. S7), at time scales $t > 2$ ps its decay becomes markedly slower (Supplemental Fig. S7), especially at high salt concentrations and low temperatures. Except at very long times, we find that the slow decay of the EFG ACFs can be described with a two-exponential fit (Supplemental Fig. S8). At the lowest concentration considered $c = 0.06$ m and $T = 25^\circ$C, the two processes have time constants $\tau_1 \approx 0.5$ and $\tau_2 \approx 2$ ps.

Interestingly, as seen in Supplemental Fig. S9 and with black dots in Fig. 2, we find that the slow decay of the EFG ACFs can be approximated equally well using a stretched exponential $\sim e^{-(t/\tau_s)^\beta}$ with $\beta = 0.67 \pm 0.05$ that we obtained from the data at the lowest concentration. By fixing the value of $\beta$ and $\tau_1$, most of the EFG ACF decay can be described with a two-parameter fit $C_{EFG}(t)/C_{EFG}(0) = (1 - \alpha_s) e^{-t/\tau_1} + \alpha_s e^{-(t/\tau_s)^\beta}$, where $\tau_s$ is the time scale of the stretched exponential decay and $\alpha_s$ is its relative weight (Supplemental Fig. S10). Note that $\tau_2$ is obtained with a double-exponential fit of $C_{EFG}(t)/C_{EFG}(0)$ discussed above and changes only by few percent from 62 fs with respect to $c$ and $T$ (see also the additional discussion in Supplemental Sec. II C). The resulting effective EFG correlation times obtained by in-
FIG. 3. **Concentration and temperature dependence of relaxation rates.** (a), Longitudinal NMR relaxation rate $T_1^{-1}$ as a function of the salt concentration $c$ as obtained in experiments (E, solid lines and open symbols) and simulations (S, filled symbols) for different temperatures. (b), Dependence of $T_1^{-1}$ on the temperature $T$ as obtained in experiments (E, solid lines and open symbols) and simulations (S, filled symbols) for different salt concentrations. The error bars for simulation results in (a) and (b) are associated with the approximation for incorporating the electron cloud contribution to the EFG (see Sec. III A).

Integrating the above expression are in excellent agreement with MD data (Supplemental Fig. S10). Finally, irrespective of the exact functional form of the slow process in the EFG ACF, both a sum of multiple exponentials or a single stretched exponential, which suggests a broad distribution of contributing relaxation modes (Supplemental Fig. S11), highlight the presence of a collective pathway behind the EFG relaxation.

Despite the fact that most of the decay of the EFG ACFs (more than two decades with respect to their initial value $C_{EFG}(0)$) can be described well with the above-discussed relations, we find that the relaxation of the long-time tail of the ACFs occurs systematically slower than the fits at intermediate times (Supplemental Figs. S10 and S11), especially at high salt concentrations and low temperatures. To illustrate such behavior, in Fig. 2(d) we show the temperature dependence of $C_{EFG}(t)$ at $c = 4$ m on a log-log scale. Although observed over a limited time range (up to a decade), the long-time relaxation of the EFG ACFs is consistent with a power law $\sim t^{-5/2}$. The latter is further highlighted in Fig. 2(e), where we plot $C_{EFG}(t)$ multiplied by $t^{5/2}$ at long times. The presence of such a hydrodynamic tail was predicted by a mode-coupling theory of Bosse et al. for the EFG ACF in molten salts [27]. This algebraic decay originates from the coupling between the motion of an ion and shear excitations in the liquid, a mechanism that causes the well-known $\sim t^{-3/2}$ tail of the velocity autocorrelation function [76]. While sampling of the EFG ACFs at even longer time scales is necessary to decisively confirm to presence of the hydrodynamic $\sim t^{-5/2}$ tail (potentially with a mesoscopic approach [77, 79]), our results for Na$^+$ in Fig. 2(d) suggest that its relative contribution may be marginal because the apparent onset of the algebraic decay occurs at time scales when the ACF has decayed by more than two decades relative to its initial value. Finally, the latter observation might give confidence in simpler approaches for the EFG relaxation that only focus on the coupling between the ionic motion and density fluctuations in the liquid, but neglect that due to coupling to shear excitations [26], as well as on those that treat the dielectric medium as a continuum [25].

### C. Quadrupolar relaxation rates

The combination of dynamic EFG fluctuations captured at the classical level (Sec. III B) and the approximation for the electron cloud contribution to the EFG to obtain accurate values of the QCC (Sec. III A) allows us to consistently evaluate the quadrupolar NMR relaxation rates for $^{23}$Na$^+$. In particular, in the present semi-classical approach, $1/T_1$ is proportional to the product of the effective correlation time of EFG fluctuations, $\tau_c = C_{EFG}(0) \int_0^\infty dt C_{EFG}(t)$, and the EFG variance (see Eq. (3)), which is approximated as $\langle V^2 \rangle = (1 + \gamma_{\text{off.}}^2 \langle V_{\text{ext}}^2 \rangle)$ with $\gamma_{\text{off.},0}^2 = 12.09$ (see Sec. III A). Note that the value of $\langle V_{\text{ext}}^2 \rangle$ is the EFG ACF $C_{EFG}(t)$ at $t = 0$, whereas the integration of $C_{EFG}(t)$ over tens of picoseconds is necessary to obtain well-converged correlation times $\tau_c$ (Supplemental Fig. S12), notably at high salt concentrations and low temperatures where a marked
slowing down of the EFG fluctuations occurs (Fig. 2). Finally, here we assume that the longitudinal rate $1/T_1$ of $^{23}\text{Na}^+$ is almost entirely determined by the quadrupolar interaction, whereas possible contributions from the dipole-dipole coupling between the spin of the $^{23}\text{Na}$ nucleus and that of $^1\text{H}, ^{23}\text{Na}, ^{35}\text{Cl}$ are neglected. While the dipole-dipole contributions to the rate can also be consistently evaluated in MD simulations [80], our estimates in Supplemental Sec. ID indicate that their effect on the NMR rate of $^{23}\text{Na}^+$ is likely to be marginal.

The semi-classical approach put forward here enables reaching a good quantitative agreement between the calculated and experimentally measured quadrupolar NMR rate $1/T_1$ for $^{23}\text{Na}^+$ that we compare in Fig. 3 with filled symbols and solid lines, respectively. As we find both in the simulations and experiments, $1/T_1$ grows with increasing the salt concentration $c$ (Fig. 3(a)) and with reducing the temperature $T$ (Fig. 3(b)), suggesting that the dynamic slowing down of EFG fluctuations (Fig. 2) is primarily responsible for the rate behavior. Experimentally, the NMR rate rises by about 50% within the considered range of concentrations $c\approx0.17–6.0\,\text{m}$ for all temperatures $T=20–50\,\degree\text{C}$ (Fig. 3(a)), in line with the previous results for $^{23}\text{Na}^+$ in aqueous NaCl [24, 30, 34]. In particular, at $T=30\,\degree\text{C}$, $1/T_1$ increases from around 15.9 s$^{-1}$ at $c=0.17\,\text{m}$ to 25.2 s$^{-1}$ at $c=5.1\,\text{m}$. With increasing $T$ from 25 to 50 $\degree\text{C}$, $1/T_1$ reduces by more than 25% for the considered salt concentrations (Fig. 3(b)). In general, our computational results for $1/T_1$ of $^{23}\text{Na}^+$ agree well with the experimental data, especially at lower salt concentrations $c\lesssim2.5\,\text{m}$, reproducing both the concentration and temperature behavior. For higher salt concentrations, we find that $1/T_1$ grows systematically faster with increasing $c$ as compared to the experiments, yet the relative error remains less than 15% over the considered range of conditions. The latter difference is likely caused by the fact that the Madrid-2019 FF captures the dynamic properties of the aqueous NaCl solution only semi-quantitatively at high salt concentrations for $c\gtrsim2\,\text{m}$ [51]. This finding is not surprising as the force field was not designed to match experiments under high concentration conditions. Nevertheless, the currently-employed approach that combines the sampling of EFG fluctuations at the classical level with the QCC parametrized with ab initio calculations for a single ion in water provides sufficient accuracy for the calculated $1/T_1$ of $^{23}\text{Na}^+$, enabling us to utilize the available microscopic information in molecular simulations to shed light on the mechanisms behind the quadrupolar relaxation.

**D. Microscopic parameters of the relaxation**

To quantify the role of dynamic and static effects that are reflected in the changes of $\tau_c$ and $\langle V^2 \rangle$, in Fig. 4 we show their dependence on the salt concentration and temperature, as extracted from MD simulations of aqueous NaCl solutions. Interestingly, opposite trends are found for the behavior of these two quantities. While $\tau_c$ increases by a factor of $\sim1.5–2.5$ with increasing $c$ and decreasing $T$ within the considered range of concentrations ($c=0.06–4\,\text{m}$) and temperatures ($T=10–50\,\degree\text{C}$), as seen in Figs. 4(a) and 4(b), the value of $\langle V^2 \rangle$ features at the same time only a relatively small reduction that does not exceed 10% of its initial value (Figs. 4(c) and 4(d)). Qualitatively the same behavior is found for the $^{23}\text{Na}^+$ relaxation in other electrolyte solutions (Supplemental Fig. S15). The latter findings unambiguously show that it is the slowing down of EFG fluctuations at the $^{23}\text{Na}$ position, resulting in augmented effective correlation times (2), that causes a marked increase in the quadrupolar NMR relaxation rate $1/T_1$ with increasing $c$ and decreasing $T$ (Fig. 3).

Within the range of considered $c$ and $T$, the effective EFG correlation time $\tau_c$ in Eq. (2) attains values that are typically well below 1 ps (Fig. 4(a) and 4(b)). The shortness of the EFG correlation time for hydrated $^{23}\text{Na}^+$ ions was already pointed out in previous classical [20, 22, 42, 45] as well as ab initio [37, 39] MD studies.
At $T = 25 \, ^\circ C$, we find that $\tau_c \approx 0.41$ ps at the lowest concentration and increases to about 0.65 ps at $c = 4$ m. The ab initio MD simulations of Philips et al. [29] for the quadrupolar relaxation of a single aqueous Na$^+$ ion yield $\tau_c = 0.42$ ps and $\langle V^2 \rangle = 2.83 \times 10^{-12} \, V^2 \cdot m^{-4}$ at comparable conditions. At $c = 0.06$ m, we find that $\tau_c$ increases from around 0.28 to 0.54 ps, a time scale that is approximately 11-14 times smaller in comparison to the average water dipole reorientation time $\tau_{\text{dip}} = \int_0^\infty dt \langle P_1[u(t) - u(0)] \rangle$ (Supplemental Fig. S14) [31, 32]. Above, $u$ is a unit vector pointing along the direction of the water molecule’s dipole and $P_1(x) = x$ is the first Legendre polynomial.

The detailed information about the EFG dynamics (Fig. 2) allows us to evaluate relative contributions of the fast and slow EFG relaxation modes to the effective correlation time $\tau_c$. Here, we will rely on the stretched exponential fits of the normalized EFG ACFs, $C_{\text{EFG}}(t)/C_{\text{EFG}}(0) = (1 - \alpha_s) e^{-t/\tau_c} + \alpha_s e^{-t/\tau_s} \mu$, discussed in more detail in Sec. II B and Supplemental Sec. II C, although qualitatively similar conclusions can be reached with other fitting schemes. We find that the slow mode contribution to $\tau_c$, given by the integral $\alpha_s \int_0^\infty dt \langle P_1[u(t) - u(0)] \rangle = \alpha_s \tau_s \beta s^{-1} \Gamma(\beta - 1)$ with $\Gamma(x)$ denoting the gamma function, yields more than 85% of its overall value and grows with increasing $c$ and decreasing $T$ (Supplemental Fig. S10(d)). This again exemplifies the governing role of the collective relaxation pathway in the quadrupolar NMR relaxation of Na$^+$ in aqueous electrolytes.

The changes in the EFG variance $\langle V^2 \rangle$, which determines the strength of the quadrupolar relaxation, are typically associated with the modification of the hydration shell structure and its symmetry [23, 31, 47]. For example, Versmold [31] demonstrated that the EFG at the position of a solute embedded into a dipolar liquid profoundly depends on the symmetry of the solvation shell and can be significantly reduced due to mutual cancellations for highly symmetric arrangements (e.g., in the case of tetrahedral or octahedral solvation shell structures). Furthermore, as the EFG is a rather short-range quantity that is proportional to $r^{-3}$ and $r^{-4}$ at the distance $r$ away from a point charge and dipole, respectively, the dominant contribution to $\langle V^2 \rangle$ is due to molecules located in the immediate neighborhood of the solute [40].

To elucidate the effect of the solvation shell structure of Na$^+$ on the EFG variance at its position, in Fig. 5 we consider $\langle V^2 \rangle$ as a function of radial distance away from the ion as well as $\langle V^2(N_w) \rangle$ averaged over configurations with a different number of water molecules $N_w$ in its first solvation shell for different concentrations and temperatures. More precisely, as seen in Figs. 5(a) and 5(b), the $c$- and $T$-dependence of $\langle V^2 \rangle$ was computed from water molecules and ions located within a different number of solvation shells around a Na$^+$ ion in comparison to the full variance evaluated by means of Ewald summation. Consistently with the case of infinite dilution [40], the first solvation shell provides the dominant contribution to $\langle V^2 \rangle$ also in the concentrated regime (more than 80%), yet a quantitative agreement is only achieved by considering the contributions from more than two solvation shells. Interestingly, opposite trends are found for the concentration and temperature behavior when the first hydration shell contribution is compared against the overall variance. While both of them increase with $T$ (Fig. 5(b)), suggesting that the temperature effect is primarily caused by enhanced thermal fluctuations, $\langle V^2 \rangle$ coming from the first shell increases in contrast to the entire value that features a small decrease with the salt concentration (Fig. 5(a)). Furthermore, the trend of $\langle V^2 \rangle$ decreasing with $c$ is only recovered by including the contributions of three and more hydration layers that correspond to particles within a radius of $r \gtrsim 8$ Å around a Na$^+$ ion, approximately the length scale at which pronounced ion-ion and ion-solvent correlations are preserved (Supplemental Figs. S4 and S5). In summary, despite the fact $\langle V^2 \rangle$ is dominated by the first solvation shell contribution, the electrostatic cancellation effects that arise beyond the first hydration layer are necessary to take into account to achieve a quantitative understanding of $\langle V^2 \rangle$ and, thus, the QCC.

**FIG. 5. EFG variance in relation to the changes in the solvation shell structure of Na$^+$ ions.** EFG variance, $\langle V^2 \rangle$, evaluated from the water molecules and ions located within a different number of solvation shells as a function of (a) the salt concentration at $T = 25 \, ^\circ C$ and (b) temperature $T$ at $c = 1$ m. Probability $P(N_w)$ of finding $N_w$ water molecules in the first solvation shell of Na$^+$ ions for (c) increasing the salt concentration at $T = 25 \, ^\circ C$ and for (d) decreasing temperature at $c = 1$ m. EFG variance corresponding to the states that contain $N_w$ water molecules in the first solvation shell, $\langle V^2(N_w) \rangle$, relative to $\langle V^2 \rangle$, for (e) increasing $c$ and (f) decreasing $T$. 

In Figs. 5(c)-(f), we further explore the effect of the first hydration layer structure and its symmetry on the resulting EFG variance at the Na\(^+\) position. The sodium ion has a quite small ionic radius of 1.02 Å that results in strong interactions with neighboring water molecules and the development of multiple coordination shell structures \[72, 82\]. As seen in Figs. 5(c) and 5(d) and as discussed in Refs. \[72, 82\], the latter are dominated by the square pyramidal and triangular bipyramidal complexes coordinated by \(N_w = 5\) water molecules, as well as by the 6-coordinated square bipyramidal state. The much less likely tetrahedral structures with \(N_w = 4\) are also present. In agreement with recent machine learning based simulations parameterized on the strongly constrained and appropriately normed functional \[72, 82\], we find that the hydration shell state with \(N_w = 6\) is the most likely at low salt concentrations, yet is becoming somewhat less probable with increasing \(c\) at the expense of tetrahedral structures with \(N_w = 4\) as well as complexes with \(N_w = 5\) (Fig. 5(c)). The latter rearrangements are due to ions that are more likely to penetrate into the first two sodium’s hydration shells with increasing \(c\) (see Supplemental Sec. II B). Qualitatively similar trends are seen with decreasing \(T\) (Fig. 5(d)). Consistently at different concentrations and temperatures, we find that the octahedral hydration complexes formed by 6 water molecules in the first solvation shell feature a reduced value of the EFG variance at the Na\(^+\) position relative to the ensemble average \((\langle V^2 \rangle)\) (Figs. 5(e) and 5(f)). While consistent with the Versmold’s symmetry argument \[81\], the magnitude of the reduction at hand does not exceed 10\% in comparison to \((\langle V^2 \rangle)\). Furthermore, the EFG variance computed for less coordinated polyhedra with \(N_w = 4\) and \(5\) are about 10\% larger than \((\langle V^2 \rangle)\). This highlights that the changes of the QCC in different Na\(^+\) hydration complexes are rather small within the considered range of salt concentrations and temperatures. Nonetheless, the trend of the variance reduction in sodium’s octahedral hydration complexes can be understood on the basis of EFG cancellations in highly symmetric environments \[81\].

Having now quantified the changes in the microscopic EFG relaxation parameters in MD and validated the resulting quadrupolar NMR relaxation rates against experiments, we are in the position to assess various assumptions concerning the QCC and the effective correlation time available in the literature \[16–18, 24, 84\]. We find that typical values of the QCC for \(^{23}\text{Na}^+\) in aqueous NaCl are considered to be in the range from \(4.8 \times 10^6\) to \(7.6 \times 10^6\) rad s\(^{-1}\) \[17, 84\], approximately \(3–4\) times smaller in comparison to the QCC that we obtain from our calculations (Supplemental Fig. S13). In particular, the QCC values are found to be \(C_Q = 19.87 \times 10^6\) rad s\(^{-1}\) at \(T = 25^\circ\)C and \(c = 0.06\) m, and generally in the range between \(19.10^6\) and \(20.6 \times 10^6\) rad s\(^{-1}\) for the considered salt concentrations and temperatures. The latter discrepancy is caused by the fact that previous experimental estimates of the sodium’s QCC \[16–18, 24, 84\] were derived from the assumption that the EFG decorrelation is primarily caused by translational and reorientational motion of water in the vicinity of hydrated Na\(^+\) ions and is characterized by \(\tau_c = 3–7\) ps \[84\]. The latter values of \(\tau_c\) are approximately an order of magnitude larger in comparison the measured ones (Fig. 4). It can therefore be concluded that the aforementioned modes of motion provide only a minor contribution to the observed relaxation rates.

**E. Electric field gradient dynamics and collective rotations of the hydration shell**

The ability to consistently decouple the changes in the QCC and the effective EFG correlation time, enables a more detailed analysis concerning the mechanisms underlying the quadrupolar relaxation. It has been suggested that the EFG correlation time could be determined by the dynamic viscosity of the solution, \(\eta\), through the Stokes-Einstein-Debye (SED) relation \[16, 17, 85\]:

\[
\tau^{\text{SED}}_c = \frac{4\pi \rho r_0^3}{3k_B T}
\]

where \(r_0\) is the sodium’s hydrodynamic (Stokes) radius and \(k_B\) is the Boltzmann constant. This is an enticing proposition, as it would allow determining correlation times and the QCC independently from combining experiments of relaxation rates and diffusion coefficients, with the latter enabling the estimation of the Stokes radius. In the context of quadrupolar relaxation, Eq. (6) would relate collective reorientations of the ion-water solvation complexes to model the EFG relaxation at the position of Na\(^+\) ion within the framework of Brownian rotational diffusion. As pointed out by Eisenstadt and Friedman \[34\], such a collective reorientational mechanism could provide a prevailing pathway behind the quadrupolar relaxation, assuming the rigidity of the hydration complex over a typical time scale of the EFG relaxation. While both the assumption of Brownian rotational diffusion \[87\] as well as the applicability of the hydrodynamic SED relation \[88\] are generally not expected to hold down to the molecular scale, here we will systematically explore the model \(\tau^{\text{SED}}_c\) in relation to \(\tau_c\) of the EFG, as it has been often exploited to rationalize the quadrupolar relaxation dynamics of \(^{23}\text{Na}^+\) \[16–18\].

The experimentally obtained Na\(^+\) diffusion coefficients (Fig. 6(a)) were combined with the highly accurate experimental viscosity values provided by Kestin \emph{et al.} \[89\] (Fig. 6(b)) to obtain the concentration and temperature dependent values of the sodium’s Stokes radius \(r_0\), as given by the standard Stokes-Einstein relation:

\[
D = \frac{k_BT}{6\pi \eta r_0}.
\]

The latter permits to consistently capture the effect of enhanced dielectric friction of such small solutes as Na\(^+\) in water \[89\]. In addition, in Figs. 6(a) and 6(b) we compare the experimental diffusion coefficients and viscosity
FIG. 6. Modeling quadrupolar relaxation with a collective rotational mechanism. (a), Diffusion coefficient of Na\(^+\) as a function of the salt concentration \(c\) for different temperatures \(T\) in experiments (solid lines with open symbols, legend shown in (a)) and simulations (filled symbols, legend shown in (b)). (b), Dynamic viscosity of the solution as a function of \(c\) for different \(T\) in experiments (solid lines with open symbols, legend shown in (a)) and simulations (filled symbols, legend shown in (b)). Experimental viscosities were taken from Ref. [85]. (c), Effective rotational correlation time \(\tau_{\text{SED}}^c\) extracted from the experimental data using the Stokes-Einstein-Debye relation (6). (d), Experimental hydrodynamic radius \(r_0\) of Na\(^+\) as calculated using the Stokes-Einstein relation (7). (e), Correlation time \(\tau_{\text{exp}}^c\) of EFG fluctuations as extracted from experimental relaxation rates \(T_{1}^{-1}\) using the QCC obtained in simulations (Supplemental Fig. S13). (f), EFG correlation time \(\tau_{\text{exp}}^c\) from (e) shown as a function of \(\eta/k_B T\) for different temperatures. Different symbols and colors correspond to the same \(T\) as in the legend of (a). \(r_{\text{eff}}^0\) is the effective hydrodynamic radius of a Na\(^+\) ion extracted under assumption that \(\tau_{\text{exp}}^c\) can be modeled by a SED model (8) (the gray line shows the best fit).

(solid lines with open symbols) against the ones that we obtained in our MD simulations (filled symbols). As the increase of the quadrupolar NMR rate of Na\(^+\) (Fig. 3) is primarily governed by the slowing down of EFG dynamics (Fig. 4), it is important that the FF in MD accurately captures dynamic properties of the electrolyte solution. More specifically, the NaCl solution viscosity was calculated using the Green-Kubo relation [90], whereas the Na\(^+\) diffusion coefficients were extracted from the long-time limit of the ion’s mean-square displacement and corrected for finite-size effects using the Yeh-Hummer formula [91] (see more details in the Supplemental Sec. I C). The above-mentioned dynamic properties in the used Madrid-2019 FF [60] are in good agreement with the experiments, capturing both the concentration and temperature behavior. \(\eta\) in MD is in nearly quantitative agreement with the experiments for low salt concentrations \(c \lesssim 2\) m, whereas increases faster than in the experiments for \(c > 2\) m, as already pointed out in Ref. [81] (Fig. 6(b)). Such more viscous behavior of the simulated NaCl at higher salt concentrations likely causes a somewhat reduced diffusivity of Na\(^+\) ions (Fig. 6(a)) as well as a more rapid increase in the simulated NMR relaxation rates with increasing \(c\) (Fig. 6(a)). Nevertheless, the relative error of MD results for \(D\) and \(T_{1}^{-1}\) are less than 10-15% of the experimental values, again giving confidence in the employed approach.

The SED correlation times \(\tau_{\text{SED}}^c\) (Fig. 6(c)), calculated on the basis of state-dependent Stokes radii \(r_0(c,T)\) (Fig. 6(d)), are compared against the effective correlation time of EFG fluctuations \(\tau_{\text{exp}}^c\) (Fig. 6(e)) that we obtained from the experimentally measured NMR rates using the sodium’s QCC from simulations (Supplemental Fig. S13) rather than those from previous estimates [16,18,24,84]. Because of a good agreement between the rates in simulations and experiments (Fig. 3), \(\tau_{\text{exp}}^c\) in MD is in nearly quantitative agreement with \(\tau_{\text{exp}}^c\), yet for consistency we distinguish these values. The calculated values of the Stokes radius decrease with increasing the salt concentration and temperature. At \(T = 25\) °C,
the experimental value of \( r_0 \) decreases from around 2.02 Å at \( c = 0.17 \) m to 1.69 Å at \( c = 6.0 \) m. Accordingly, \( \tau_{c}^{\text{SED}} \) increases from around 7.5 to 8.6 ps, larger by more than one order of magnitude than \( \tau_{c}^\text{exp} \), which grows from 0.44 to 0.73 ps. Despite the fact that both \( \tau_{c}^{\text{SED}} \) and \( \tau_{c}^\text{exp} \) lengthen with increasing \( c \) and decreasing \( T \), as seen from the color maps in Figs. 6(c) and 6(e), \( \tau_{c}^{\text{SED}} \) exceeds \( \tau_{c}^\text{exp} \) by a factor of 8-17. Furthermore, note that the SED used here rather serves as a lower bound for the rotational correlation time of the hydration complex, as its hydrodynamic size is highly likely larger than that of the sodium ion. Thus, we conclude that the collective hydration shell rotations do not constitute the prevailing pathway behind the quadrupolar relaxation and the EFG correlation times cannot be understood on the basis of the Stokes-Einstein-Debye relation (6) parameterized using the translational hydrodynamic radius of sodium ions (6).

This is further illustrated in Fig. 7(f) that shows \( \tau_{c}^\text{exp} \) plotted as a function of \( \eta/k_B T \) for various temperatures. While a Stokes-Einstein-like relation holds for \( \tau_{c}^\text{exp} \), meaning that a strong correlation \( \tau_{c}^\text{exp} \propto \eta/k_B T \) exists within the considered range of system parameters, the effective Stokes radius \( r_{0}^\text{eff} = 0.69 \) Å that would correspond to the EFG correlation time \( \tau_{c}^\text{exp} \) within the Stokes-Einstein-Debye model (6) is clearly unphysical and smaller than the ion size. The resulting value of \( \tau_{c}^\text{exp} \) was obtained from the fit

\[
\tau_{c}^\text{exp} = \frac{4\pi\eta r_{0}^\text{eff}^3}{3k_B T} + \tau_{c}^\text{eff}
\]

with an additional small intercept \( \tau_{c}^\text{eff} = 0.11 \) ps needed for the best data representation (8). Finally, the validity of the relation \( \tau_{c}^\text{exp} \propto \eta/k_B T \) for the correlation time of EFG fluctuations demonstrated in Fig. 6(f) serves as an explanation for the correlation found between \( \tau_{c}^\text{exp} \) and \( D^{-1} \) reported in Refs. [16–18], rather than simplified assumptions of rotational Brownian diffusion that yield much larger estimates for \( \tau_{c}^\text{exp} \) (see Figs. 6(c) and 6(e)).

F. Quadrupolar relaxation as a local probe of the collective dynamics in electrolytes

Increasing the salt concentration and decreasing temperature makes the solutions more viscous, thereby decelerating microscopic dynamics of molecules that impact both the water reorientation as well as motions driving the quadrupolar relaxation. To illustrate the relationship between these effects, in Fig. 7 we extract typical times of structural relaxation from the ACFs of the stress tensor \( C_{\text{stress}}(t) \) in our MD simulations. Similarly to the case of pure water [92], the short-time behavior of the stress ACFs that corresponds to elastic, vibrational contributions feature little changes with varying \( c \) and \( T \). On the other hand, as seen in Fig. 7(a), the long-time tail of the ACF slows down with increasing \( c \) and decreasing \( T \), indicating an overall deceleration of the viscous dynamics of the liquid. Similarly to the relaxation of electric field gradients at the position of \( \text{Na}^+ \), we find that the long-time tail of the stress ACF can be model well with a stretched exponential, \( \sim e^{-t/\tau_K} \), with \( \beta_K \approx 0.61 \pm 0.04 \), and \( \tau_K \) attaining values between 0.13 and 0.70 ps for the range of considered system parameters. The obtained value of \( \beta_K \) is consistent with the case of pure water, as compared to MD simulations with a flexible simple point charge polarizable model (SPC/Fw) [92] as well as time-resolved spectroscopy experiments [93]. The mean time of the structural relaxation that we define as the integral of the stretched exponential expression, \( \tau_{\text{struct}} = \tau_K \beta_K^{-1} \Gamma(\beta_K^{-1}) \), increases both with increasing \( c \) and decreasing \( T \), indicating an overall slowing down of the dynamics (see inset of Fig. 7(a)).
We now return to the microscopic time scales of molecular motion in relation to \( \tau_{\text{struct}} \). As discussed above, the mean reorientation time of a water dipole \( \tau_{\text{dip}} \), assumed to drive the quadrupolar relaxation within the Hertz model \([28, 29]\), is considerably larger than the EFG correlation time \( \tau_c \). Yet, both \( \tau_{\text{dip}} \) and \( \tau_c \) increase similarly with increasing \( c \) and decreasing \( T \), as seen from the strong correlation between the latter two quantities in Fig. 7(b). This shows that the deceleration of the electrolyte solution dynamics, marked by an enhanced viscosity, impacts in a similar way both the motions that drive water reorientation as well as those that cause the relaxation of electric field gradients at the ion position. The latter is finally exemplified in Fig. 7(c) that shows \( \tau_{\text{struct}} \) plotted against \( \tau_c \), with the latter two quantities being again profoundly correlated and, remarkably, quite close to each other, both lying in the subpicosecond domain. Furthermore, the facts that both of these integrated time scales do not differ considerably and that \( \tau_c \) is dominated by the long-time tail of the EFG ACF (Supplemental Sec. II C) indicates that the microscopic time parameters of the respective stretched exponentials are also similar. While the stress and EFG tensors are not directly related to each other, both quantities are inherently collective, the relaxation of their fluctuations is mainly driven by many-body correlations and occurs similarly for \( t \gtrsim 0.4 \) ps; in addition, their mean relaxation times are quite close to each other. All these observations suggest that the fast collective motions of the liquid that drive the solution structural rearrangements are primarily responsible for the quadrupolar NMR relaxation. Finally, the closeness of \( \tau_{\text{struct}} \) and \( \tau_c \) offers an additional explanation for the failure of isotropic models for the EFG relaxation, e.g., those based on the Stokes-Einstein-Debye relation. The notion of continuous solvent description that is rooted in Eq. (6) assumes that the microscopic stress fluctuations occur on time scales much shorter than that of the EFG relaxation, that is \( \tau_c \gg \tau_{\text{struct}} \). On the contrary, that is clearly not the case for the EFG correlation time, leading to the coupling between viscous dynamics of the liquid and EFG relaxation on the subpicosecond time scales and above.

**IV. CONCLUSIONS AND PERSPECTIVES**

We have shown that the multiscale methodology combining DFT PAW calculations to parameterize the QCC and classical MD simulations to sample long-time EFG fluctuations enables an accurate description of the concentration and temperature behavior of the quadrupolar NMR relaxation rates of \(^{23}\)Na\(^+\) in aqueous electrolyte solutions. The resulting NMR rates are in very good agreement with the experimental data, especially at low salt concentrations, as validated in aqueous NaCl at multiple concentrations and temperatures. Furthermore, the qualitative trends are also in alignment up to the saturation concentration as well. Such a good agreement then motivated a more detailed analysis of the microscopic mechanisms behind the quadrupolar relaxation. Qualitatively similar to the infinite dilution case \([21, 22, 39, 45]\), the EFG relaxation occurs in two steps with a rapid initial decorrelation occurring at a time scale consistent with the librational water dynamics (\(\sim 60 \) fs), followed by a much slower non-exponential decay that profoundly slows down with increasing the salt concentration \( c \) or decreasing temperature \( T \). The long-time tail of EFG ACFs for Na\(^+\) is consistent with an algebraic tail \( \sim t^{-5/2} \), yet observed here for a limited time period, as predicted by a mode-coupling theory developed for the EFG relaxation in molten salts \([27]\). We find that the growth of the relaxation rate \( T_j^{-1} \) with increasing \( c \) and decreasing \( T \) is primarily due to the slowing down of the EFG fluctuations reflected in the augmented EFG correlation time \( \tau_c \), while the concurrent changes in the QCC are rather small. Within the range of considered system parameters, the changes in \( \tau_c \) are driven by the slow decay of the EFG ACF, highlighting a collective origin behind the observed effect.

We have assessed the validity of several simple, commonly assumed relaxation models for \( \tau_c \). We find that both the mean water dipole reorientation time \( \tau_{\text{dip}} \), which arises in the Hertz models of the EFG relaxation \([28, 30]\), as well as the rotational correlation time \( \tau_{\text{SED}} \) associated with a Stokes-Einstein-Debye process \([16, 18, 35]\), as related to collective rotations of the ion’s hydration complex, overestimate the consistently determined \( \tau_c \) by at least an order of magnitude. Ultimately, such a disagreement is understandable as both of these models restrict the description of dynamic relaxation processes to one- and two-body correlation terms, respectively. In relation to the EFG at the ion position that is an inherently collective quantity, the latter is a great oversimplification and the inclusion of three- and higher-order interparticle correlations is necessary to appropriately capture the EFG dynamics \([31, 33]\). The quantitative interpretation of the EFG correlation times in terms of such simple isotropic models should therefore be used with caution.

We have demonstrated that the growth of \( \tau_c \) with increasing the salt concentration and decreasing temperature, leading to the same behavior of the quadrupolar NMR rate of \(^{23}\)Na\(^+\), is associated with the overall deceleration of the electrolyte dynamics and yields a correlation of \( \tau_c \) with \( \eta/k_BT \). On the microscopic side, we find that \( \tau_c \) is strongly correlated with a mean time scale of structural relaxation of the solution, \( \tau_{\text{struct}} \), that we extracted from the intermediate- and long-time relaxation of the stress tensor. The stress and EFG tensors are both collective quantities and the relaxation of their fluctuations occurs in a similar fashion in the picosecond domain. Moreover, the closeness of the mean correlation times of both quantities that lie in the THz regime suggest that the short-time, collective, structural relaxation processes in the liquid are primarily responsible for the quadrupolar NMR relaxation of \(^{23}\)Na\(^+\). We note that the close agreement between \( \tau_c \) and \( \tau_{\text{struct}} \) may pertain to the
small size of the sodium ion, and may differ in the case of larger quadrupolar solutes. Nonetheless, our previous results for \( \tau_c \) calculated for other quadrupolar ions (e.g., \(^7\)Li\(^+\), \(^{39}\)K\(^+\), etc.) in water at infinite dilution similarly yielded values below a picosecond \([20]\). Such shortness of the EFG relaxation that occurs on time scales comparable to \( \tau_{\text{struct}} \) hence explicitly invalidates the assumptions of continuous hydrodynamic approaches. The current results thus suggest that the quadrupolar \(^{23}\)Na\(^+\) NMR relaxation expected of may be used as a complementary tool to analyze the electrolyte dynamics in the THz domain. Given the advantage that the quadrupolar relaxation dynamics is largely determined by the processes in the immediate vicinity of the solute (first few solvation shells), it can be used as a supplementary method to probe fast, short-range, molecular motions in the ionic solvation cages that have been associated with the high-frequency dielectric response and macroscopic conductivity of aqueous electrolytes \([92]\), as well as water structural relaxation \([92]\).

Our work thus paves the way for a better description and understanding of the quadrupolar NMR relaxation experiments. The ability to capture the respective NMR rates by means of classical MD allows shedding light on the quadrupolar phenomena that occur in heterogeneous multicomponent environments, such as concentrated aqueous solutions of multiple salts or polyelectrolytes, where the relaxation dynamics may be influenced by interface formation, microphase separation, or ion binding to polyelectrolyte chains \([95, 96]\). Future work should also focus on the development of mesoscopic approaches that would allow a quantitative description of quadrupolar relaxation in complex biological-type compartments, characterized either by slow-motion conditions with dynamics within intracellular and extracellular spaces in biological tissues that may include structural anisotropy with residual quadrupolar coupling and a distribution of correlation times (as in articular cartilage where sodium ions are surrounded by a collagen matrix). This approach would be helpful in assessing cellular or cartilage integrity in many pathologies that can be probed with sodium magnetic resonance relaxation and imaging in vivo \([4, 97]\).

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