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journal homepage: www.elsevier.com/locate/ssnmrInterpretation of ^1H and ^2H spin–lattice relaxation dispersions: Insights from molecular dynamics simulations of polymer melts

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ABSTRACT

We demonstrate that molecular dynamics simulations are a versatile tool to ascertain the interpretation of spin–lattice relaxation data. For ^1H , our simulation approach allows us to separate and to compare intra- and inter-molecular contributions to spin–lattice relaxation dispersions. Dealing with the important example of polymer melts, we show that the intramolecular parts of ^1H spectral densities and correlation functions are governed by rotational motion, while their inter-molecular counterparts provide access to translational motion, in particular, to mean-squared displacements and self-diffusion coefficients. Exploiting that the full microscopic information is available from molecular dynamics simulations, we determine the range of validity of experimental approaches, which often assume Gaussian dynamics, and we provide guidelines for the determination of free parameters required in experimental analyses. For ^2H , we examine the traditional methodology to extract correlation times of complex dynamics from relaxation data. Furthermore, based on knowledge from our computational study, it is shown that measurement of ^2H spin–lattice relaxation dispersions allows one to disentangle the intra- and inter-molecular contributions to the corresponding ^1H data in experimental work. Altogether, our simulation results yield a solid basis for future ^1H and ^2H spin–lattice relaxation analysis.

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1. Introduction

NMR is a versatile tool to investigate molecular dynamics. The detailed interpretation of the experimental data, however, depends on the probe nucleus. For example, ^2H NMR yields insights into rotational motions of molecules [1–3], while ^7Li NMR provides access to translational motions of ions [4–6]. For these probe nuclei, the resonance frequencies are determined by the quadrupolar interaction and, due to the single-particle nature of this interaction, single-particle correlation functions are obtained. In ^1H NMR, the homonuclear dipole–dipole interaction governs experimental findings and, consequently, intra- and inter-molecular contributions to the resonance frequency exist [7]. This means that the observed correlation functions depend on single-particle and multi-particle effects. Hence, ^1H NMR data contain a wealth of information, but disentanglement of different contributions can be difficult.

For various probe nuclei, spin–lattice relaxation (SLR) was analyzed to study molecular dynamics. Conventional SLR approaches determine the relaxation time T_1 at a given value of the magnetic field B_0 and, hence, at a fixed value of the resonance frequency ω . By contrast, fast field cycling (FFC) NMR allows one to

vary magnetic field and resonance frequency. In this way, it is possible to observe the frequency dependence of the relaxation time, $T_1(\omega)$, providing access to spectral densities and correlation functions [8–10]. This possibility was used to characterize dynamical processes in supercooled or confined liquids, polymer melts, biological materials, and liquid crystals [9–19].

In ^1H FFC, intramolecular contributions often outweigh inter-molecular ones due to the strong distance dependence of the dipolar interactions. Then, it is possible to interpret the experimental results in terms of autocorrelation functions of rotational motion. However, previous works [13,14,20,21] showed that, for sufficiently low resonance frequencies, inter-molecular contributions can govern the relaxation behavior. In such situation, the low-frequency data provide access to translational motion, e.g., to self-diffusion coefficients D . Thus, ^1H FFC has the potential to yield detailed insights into both rotational and translational dynamics. Quantitative analyses, however, can require model assumptions [9,10]. For example, Gaussian motion was often assumed. Also, it was argued that separation of inter- and intra-molecular contributions is possible based on dilution experiments with deuterated compounds. When studying complex dynamics in disordered systems, the validity of such presuppositions cannot be taken for granted, necessitating detailed tests.

Here, we use molecular dynamics (MD) simulations to examine common methodologies in ^1H and ^2H SLR analyses. MD simulations yield the positions of all atoms at all times, with a time

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window limited by computer power. Exploiting this knowledge to calculate ^1H and ^2H spectral densities and correlation functions, we determine which dynamical information can be extracted from SLR data. In particular, we scrutinize the possibility to study translation diffusion in ^1H FFC. Moreover, the MD data are used to quantify the importance of intra- and inter-molecular contributions to ^1H SLR. Finally, we test the relevance of common model assumptions in ^1H FFC work, such as Gaussianity. In this way, we intend to provide a solid basis for future analyses of experimental findings in ^1H and ^2H SLR studies.

Our MD studies are performed for all-atom models of polyethylene oxide (PEO) and polypropylene oxide (PPO). For both polymer melts, we consider a broad temperature range and various molecular weights M_w . For different chain lengths, we ascertain in which way glassy dynamics and polymer dynamics manifest themselves in spectral densities and correlation functions related to the SLR behavior. Thus, we restrict ourselves to the important examples of glass-forming polymer melts, but we expect that most results are transferable to other types of complex dynamics in disordered systems.

2. Methods

2.1. Molecular dynamics simulations

In MD simulations, Newton's equations of motion are numerically solved for multi-particle systems interacting via classical interaction potentials. We perform MD simulations for PEO_N and PPO_N where N denotes the number of monomer units. The studied chain lengths range from $N=2$, corresponding to a liquid composed of small molecules, to $N=150$, mimicking a melt consisting of polymer chains. The interatomic interactions in the models are described by quantum-chemistry based all-atom force fields, which enable good reproduction of thermodynamic, structural and dynamical properties of PEO and PPO melts [22,23]. In addition to nonbonded interactions, which are modeled by Buckingham and Coulomb potentials, the force fields feature terms adjusting bond lengths, bond angles, and dihedral angles. From these MD simulations, the trajectories of all atoms are obtained, i.e., the full microscopic information is available. The studied PEO and PPO systems comprise ca. 4000 atoms. Further details of our simulations can be found in previous publications [24–26].

The output of the MD simulations can be used to calculate ^1H and ^2H SLR times for the studied polymer models, see Section 2.2. For a computation of ^1H NMR data, we exploit that knowledge about the time evolution of the proton–proton internuclear vectors is available from the trajectories of the hydrogen atoms. To obtain ^2H NMR data, we do not distinguish between protonated (H) polymers and deuterated (D) polymers and assume that the rotational motions of the C–H bonds in the models determine the results in the same way as the rotational motions of the C–D bonds in the measurements or, in simple terms, we suppose for the analysis that the protons are deuterons. While there are minor quantitative differences between the dynamical behaviors of protonated and deuterated polymers, major qualitative differences are not expected.

2.2. Spin–lattice relaxation

For diamagnetic systems, ^1H SLR is governed by stochastic fluctuations of the magnetic dipole–dipole interactions between pairs of protons. It proved useful to write the relation between the

rate of the relaxation and the fluctuation of the coupling as [7]:

$$\frac{1}{T_1} = \frac{3}{2} I(I+1) \left(\frac{\mu_0}{4\pi}\right)^2 \gamma^4 \hbar^2 [J^{(1)}(\omega) + J^{(2)}(2\omega)] \quad (1)$$

Here, I and γ are the nuclear spin and the gyromagnetic ratio of the proton, respectively. Moreover, the spectral densities $J^{(m)}(\omega)$ are defined by the relations

$$J^{(m)}(\omega) = 2 \operatorname{Re} \int_0^\infty G^{(m)}(t) \exp(-i\omega t) dt \quad (2)$$

$$G^{(m)}(t) = \sum_k \langle F_{jk}^{(m)}(0) F_{jk}^{(m)*}(t) \rangle \quad (3)$$

$$F_{jk}^{(m)}(t) = d_m \frac{Y_{2m}(\Omega_{jk}(t))}{r_{jk}^3(t)} \quad (4)$$

The time-dependent internuclear vector connecting proton j and proton k is denoted as $\mathbf{r}_{jk}(t)$. The modulus of this vector is r_{jk} and $\Omega_{jk} = (\theta_{ij}, \phi_{ij})$ specifies its orientation with respect to the direction of the external magnetic field. The normalized spherical harmonics are referred to as Y_{lm} and the angular brackets indicate an average over all pairs of protons. Apart from $J^{(1)}$ and $J^{(2)}$, the spectral density $J^{(0)}$ will be of relevance in the following. In the above equations, the constants are $d_0^2 = 16\pi/5$, $d_1^2 = 8\pi/15$, and $d_2^2 = 32\pi/15$. For isotropic systems, the correlation functions $G^{(m)}(t)$ merely differ by constant factors

$$\frac{1}{6} G^{(0)}(t) = G^{(1)}(t) = \frac{1}{4} G^{(2)}(t) \quad (5)$$

In this contribution, we will use MD simulation data to determine whether these relations, which are often used for an analysis of experimental results, are fulfilled for polymer melts. To keep the following considerations concise, we tacitly assume isotropic systems and skip the superscript (m) for the moment.

From Eq. (3), it is clear that both intra- and inter-molecular contributions exist. We denote the correlation function arising from protons k , which belong to the same molecule as the reference proton j , as G_{intra} , while that stemming from protons k , which reside on a different molecule, is referred to as G_{inter} . The corresponding spectral densities are denoted as J_{intra} and J_{inter} . Accordingly, the SLR rate is a sum of intra- and inter-molecular contributions [14,20]:

$$\frac{1}{T_1} = \frac{1}{T_{1,intra}} + \frac{1}{T_{1,inter}} \quad (6)$$

While rotational motion dominates the intramolecular part, translational motion manifests itself in the inter-molecular part, in particular, at long times and low frequencies [21,27]. In the following, we take a closer look at the intra- and inter-molecular parts.

The intramolecular part is dominated by glassy dynamics at sufficiently short times and high frequencies [10]. Time-domain and frequency-domain behaviors associated with glassy dynamics can be described by Kohlrausch–Williams–Watts (KWW) and Cole–Davidson (CD) functions, respectively:

$$G_{intra}(t) \propto \exp \left[- \left(\frac{t}{\tau_K} \right)^{\beta_K} \right] \quad (7)$$

$$J_{intra}(\omega) \propto \frac{\sin[\beta_C \arctan(\omega\tau_C)]}{\omega [1 + (\omega\tau_C)^2]^{\beta_C/2}} \quad (8)$$

Here, the parameters τ_K and τ_C specify the time scale of the motion and the parameters $0 < \beta_K, \beta_C \leq 1$ are employed to take into account that glassy dynamics is not characterized by exponential correlation functions. For chain-like molecules, glassy dynamics is followed by polymer dynamics at longer times and lower frequencies. In particular, Rouse dynamics leads to power laws of spectral densities and correlation functions [28]. At even longer times and

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