

Nuclear-Magnetic-Resonance Measurements Reveal the Origin of the Debye Process in Monohydroxy Alcohols

C. Gainaru,^{1,*} R. Meier,² S. Schildmann,¹ C. Lederle,¹ W. Hiller,³ E. A. Rössler,² and R. Böhmer^{1,†}

¹Fakultät für Physik, Technische Universität Dortmund, 44221 Dortmund, Germany

²Physikalisches Institut, Universität Bayreuth, 95440 Bayreuth, Germany

³Fakultät für Chemie, Technische Universität Dortmund, 44221 Dortmund, Germany

(Received 25 August 2010; revised manuscript received 26 November 2010; published 16 December 2010)

Monohydroxy alcohols show a structural relaxation and at longer time scales a Debye-type dielectric peak. From spin-lattice relaxation experiments using different nuclear probes, an intermediate, slower-than-structural dynamics is identified for *n*-butanol. Based on these findings and on translational diffusion measurements, a model of self-restructuring, transient chains is proposed. The model is demonstrated to explain consistently the so-far puzzling observations made for this class of hydrogen-bonded glass forming liquids.

DOI: 10.1103/PhysRevLett.105.258303

PACS numbers: 82.30.Rs, 76.60.Es, 77.22.Gm

The dielectric response of monohydroxy alcohols, an important class of hydrogen-bonded liquids, was treated by Debye using a model which he reviewed in his 1929 book [1]. Later, it was recognized that these alcohols, in addition to a very intense Debye process, exhibit two relaxations at higher frequencies [2,3]. The latter two are, by now, undisputedly identified as the structural and the Johari-Goldstein relaxation [4]. However, the origin of the pronounced Debye peak at low frequencies, often linked to the presence of hydrogen bonds and discussed in terms of supramolecular structures, has remained controversial. These structures manifest themselves as prepeaks in the static structure factor [5], likely due to hydrogen-bonded chains [6–8] that are most directly identified from molecular-dynamics simulations [9–11]. It is remarkable that despite continued efforts the Debye process has resisted observation using, e.g., calorimetric [12] and viscoelastic experiments [13]. For alcohols the Debye peak vanishes if two or more OH groups are in proximity on the same molecule. Interestingly, though, H₂O, often discussed in analogy to alcohols, does show a Debye-like process despite the presence of effectively two hydroxyl groups per molecule [14]. Not only the similarity to the dielectric absorption of water, but also the importance of “simple” alcohols as solvents, calls for an understanding of their microscopic dynamics.

On the basis of spin-relaxation times T_1 for *n*-butanol, a well studied glass former [3,6,8,9,15], we provide evidence for a slower-than-structural hydroxyl group dynamics using nuclear magnetic resonance (NMR). Taking into account also self-diffusion and dielectric measurements, a transient-chain model is developed which rationalizes all the perplexing features of alcohols just summarized, thus resolving a long-standing puzzle.

Figure 1 presents ¹H spin-lattice relaxation rates of *n*-butanol which was specifically isotope labeled either at its OH site [CD₃-(CD₂)₃-OH] or at its alkyl part

[CH₃-(CH₂)₃-OD]. From data recorded at a Larmor frequency ω_L , the rate maxima for the two species are seen to appear at temperatures about $\Delta T \approx 28$ K apart. Similar observations can be made from ²H- T_1 measurements, except that here, due to the larger NMR coupling constant, the ²H rates are shifted to larger values. Both probes indicate that, at a given T , the underlying molecular correlation times τ_{OH} are much slower than τ_{alkyl} [16,17].

Figure 1 includes dielectric losses $\epsilon''(\omega_L)$ measured in the T range of the Debye peak from which the time constant $\tau_D = 1/(2\pi\nu_{peak})$ can be read off. By subtracting

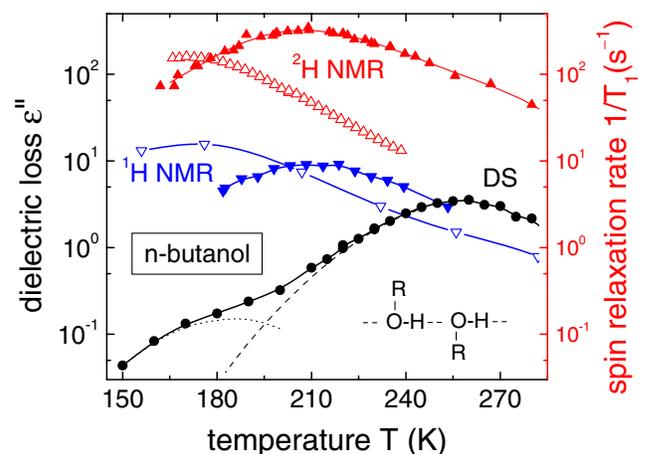


FIG. 1 (color online). Dynamic susceptibility of *n*-butanol as probed using the dielectric loss (●, 50 MHz) and NMR: ¹H- T_1 (blue ▼, $\omega_L/2\pi = 55.6$ MHz; blue ▽, 46.2 MHz) and ²H- T_1 (red ▲, red △, 55.6 MHz). The closed triangles refer to measurements at the hydroxyl group, the open triangles to those at the alkyl part of butanol. The solid lines are drawn to guide the eye. The dashed line marks the contribution of the Debye process, and after its subtraction from the total loss the dotted line, corresponding to the α process, is obtained. The inset shows a sketch of two hydrogen-bonded alkanols where R designates an alkyl group.

the contribution of the Debye relaxation, a peak due to the structural relaxation is obtained from which τ_α can be gained. From Fig. 1 it is clear that $\tau_D > \tau_{OH} > \tau_\alpha$; thus an additional intermediate, hitherto overlooked time scale exists, providing clues to identify the microscopic nature of the Debye process.

For a detailed comparison with ε'' , it is essential to determine also T_1 in broad ω_L and T ranges. In our present field cycling NMR experiments [18] on $CD_3-(CD_2)_3-OH$, ω_L was varied by more than 3 decades; see the inset of Fig. 2. These data were replotted in the susceptibility format, $\chi''(\omega) \propto \omega/T_1$. From the χ'' peaks at the lowest T , the correlation times τ_{OH} were determined on the basis of a Cole-Davidson spectral density. We obtained a very good fit employing an exponent $\beta_{CD} = 0.22$, which implies a very broad distribution of time scales [18]. The vertical shift required to obtain the practically perfect master curve shown in Fig. 2 yielded τ_{OH} for higher T . These τ_{OH} and a data point measured at room temperature [19] are collected in an Arrhenius diagram, Fig. 3, together with the time constants τ_D and τ_α from dielectric spectroscopy. The OH correlation times τ_{OH} are ~ 8 times longer than τ_α and ~ 50 times shorter than τ_D at $T \sim 160$ K.

With one proton per molecule, $^1H-T_1$ measurements are solely sensitive to *intermolecular* dynamics while 2H probes the reorientation of a single hydroxyl group. Therefore, at first glance, it appears surprising that $^1H-T_1$ and $^2H-T_1$ yield practically the same τ_{OH} . However, this similarity can be rationalized if the polar head groups aggregate in a manner sketched in Fig. 1: Then, a typical

OH bond direction is oriented approximately along the vector connecting two adjacent hydroxyl protons [20]. Thus, our measurements support the time honored notion that alcohols form chainlike structures, see, e.g., Ref. [8]. The motion of the nonpolar alkyl groups about the backbone of these structures can be mapped out via ^{13}C NMR. From T_1 measurements at the α -carbon site we determined $\tau_{CH_2} = \tau_{alkyl}$ and find $\tau_{alkyl} \approx \tau_\alpha$ [21] in accord with results for propanol [4,16].

From measurements of the self-diffusion coefficient D of *n*-butanol [21] and from those of its viscosity η [22], for $318 > T > 288$ K, we determined the hydrodynamic radius of the translationally moving moieties to be $r_H = k_B T / (6\pi\eta D) \approx 2.3$ Å. This is in good agreement with the molecular radius estimated for butanol [23] ruling out a supramolecular long-range transport. A chain motion without displacing the chain as a whole is pictured in Fig. 4. For simplicity only a single, relatively short chain is highlighted. The sequence of frames in this figure visualizes a snakelike motion induced by a successive loss (or gain) of segments at its one end and a gain (or loss) of segments at its other end. The “core” of the chain, i.e., the “inner” hydrogen-bridged hydroxyl groups, are temporarily held together by electrostatic forces which in turn are responsible for the segregation of the polar groups from the nonpolar alkyl chains.

In such a transient-chain scenario a slow dipolar, single-exponential, i.e., Debye-type process, naturally arises. The succession of the polar OH groups along the curvilinear chains yields a supramolecular dipole moment, similar to what happens in type A polymers [24]. The reorientation

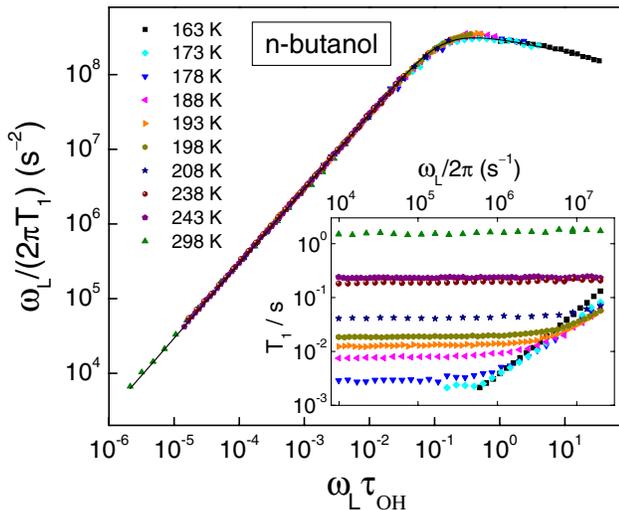


FIG. 2 (color online). The inset shows proton spin-lattice relaxation times of supercooled $CD_3-(CD_2)_3-OH$ as measured in broad ranges of T and ω_L . The main frame presents the same data in a scaled susceptibility format. The only variable required to obtain this virtually perfect master plot is the T -dependent correlation time τ_{OH} . The solid line is a fit based on a Cole-Davidson spectral density.

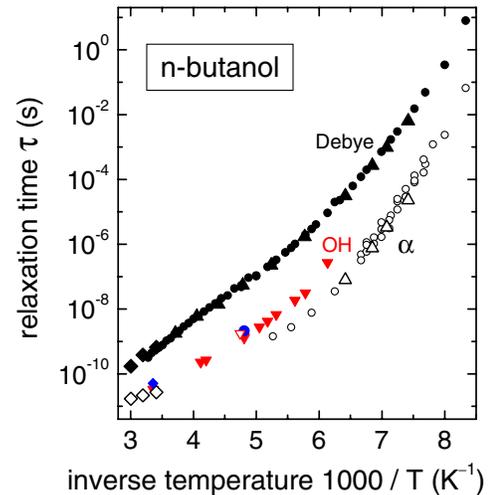


FIG. 3 (color online). Arrhenius plot of *n*-butanol including time constants from dielectric spectroscopy (some low-frequency data are from Ref. [15]) and from NMR. The present data [τ_D , ●; τ_α , ○; τ_{OH} from $^1H-T_1$, gray (red) ▼, gray (red) ▽; τ_{OH} from $^2H-T_1$, gray (blue) ●] is compared with literature values for τ_D (▲, Ref. [8]; ◆, Ref. [3]), τ_α (△, Ref. [2]; ◇, Ref. [3]) and τ_{OH} [gray (blue) ◆; Ref. [19]].

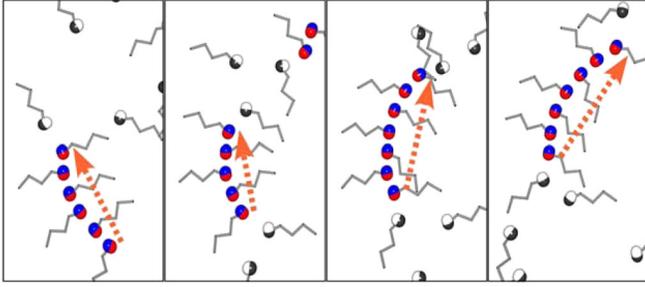


FIG. 4 (color online). Schematic illustration of the transient-chain model. Mutually bonded OH groups are shown in color (gray). The sequence of frames is meant to visualize how molecules attach to the chain and detach from it. The dotted arrows highlight the end-to-end vector of the self-restructuring, transient chain. Its reorientation, corresponding to the Debye process, is obviously very slow on the scale set by the elementary steps. The chain-length fluctuations are much faster than τ_D leading to an exponential relaxation. An animated version of this figure is available from the authors upon request.

of this moment, i.e., that of the chain's end-to-end vector is to be associated with τ_D . Since the detachment and attachment of segments is a stochastic process, chain length variations arise as time progresses. Thus, while at any given instant a distribution of chain lengths may be present, with $\tau_D \gg \tau_{OH}, \tau_\alpha$, only the mean (time-averaged) length matters on the time it takes to reorient the end-to-end vector. This precludes a time scale polydispersity due to chain length variations. Furthermore, during τ_D each chain is subject to fast environmental fluctuations. Both effects take place on a time scale of the order of τ_α leading to a single-exponential Debye relaxation on the scale of τ_D .

To visualize the situation, comparisons with type A polymers can be helpful but should not be overemphasized. One should realize that in our case higher-order end-to-end (Rouse-type) normal modes based on the existence of permanent links between chain segments are absent [24]. It may be asked how long the transient alcohol chains typically are. By assuming that “free” molecules are transported to and away from the chain ends on a time scale not too different from τ_α , the lifetime of a molecule within a chain with N segments is of the order of $N\tau_\alpha$. Considering the orientation of an OH group as essentially fixed as long as it is part of a chain, τ_{OH} is thus of the order of $N\tau_\alpha$. From Fig. 3 it can be inferred that $\tau_{OH}/\tau_\alpha \approx N$ varies between 5 and 10 in the temperature range in which both time constants are available, in good quantitative agreement with computer simulations [10,11] and x-ray investigations of the structure of monoalcohols [25].

Taking the polymer analogy one step further, the molecular dipole moment μ , typically around 1.7 D for monoalcohols [26], can be thought to be decomposed into components locally oriented along the chain (μ_{\parallel}) and perpendicular to it (μ_{\perp}). For the “segmental” motion,

which we associate with the α process, $\mu_{\perp} < \mu$ yields a reduced relaxation strength, as experimentally observed [27]. In fact, since the OC bond carries the main dipole moment in the alkyl chain, and since $\mu_{OC} \approx 0.74$ D [28], one expects that $\mu_{\perp} \approx \mu/2$. The $\mu_{\parallel} \approx \mu_{OH}$ components add up leading to a Debye process with enhanced intensity: For a chain formed by N hydrogen-bonded OH groups, each carrying $\mu_{OH} \approx 1.5$ D [28], $\mu_{\text{end-to-end}}$ is of the order of $N\mu$. The number of molecules participating in the α process is N times larger than the number of chains if for simplicity we assume that essentially all molecules are involved in both processes. Thus, the ratio between the relaxation strengths of the two processes at a given temperature is expected to be $\Delta\varepsilon_D/\Delta\varepsilon_\alpha = (\mu_{\text{end-to-end}}/\mu_{\perp})^2/N \approx 4N$. For *n*-butanol and for several other monoalcohols [4,26,29], $\Delta\varepsilon_D/\Delta\varepsilon_\alpha = 30 \pm 3$ is experimentally found. Thus, N is 7–8, in good agreement with the number obtained above from the τ_{OH}/τ_α ratio. Furthermore, from our model $\Delta\varepsilon_D/\Delta\varepsilon_\alpha$ and τ_D/τ_α are both expected to decrease for shorter end-to-end chains, also in agreement with experimental observations [21]. This in turn implies the growth of $\Delta\varepsilon_\alpha$ at the expense of $\Delta\varepsilon_D$ not only when pressure is increased [30,31], but also when temperature is increased. Our spectral analysis (not shown) confirms this nontrivial $\Delta\varepsilon_\alpha(T)$ behavior.

The present model also explains why relaxation modes corresponding to a Debye peak are not observed in mechanical spectroscopy. Because of the transient nature of the chains, the motion of the end-to-end vector does not couple to changes of the internal stress field. Near τ_D a mechanical relaxation mode is thus not expected. All but a minute decrease of the overall stiffness could result when reducing the chain length, e.g., by pressure application. Furthermore, the “wandering snakes” do not lead to energy fluctuations or to entropy fluctuations on the time scale set by τ_D . However, a minor calorimetric signature corresponding to time scales $\tau_{OH} > \tau_\alpha$ could show up [32]. Only very few methods apart from dielectric spectroscopy are sensitive to transient, dipolar chains. Other direct evidence for dynamics on the τ_D scale comes from solvation dynamics experiments [33] and from largely overlooked Kerr-effect work on monoalcohols [34].

For polyalcohols, with each molecule carrying several OH groups, branched structures will result. The unsynchronized OH switching occurring in such a multiple-branch structure then leads to an effective mutual cancellation of the component moments. Thus, with a vanishing net dipole moment a supramolecular dielectric signature does not arise from such structures and a Debye process is not expected, in harmony with the experimental situation.

It is tempting to check which modifications of the model are required to apply it also to water with its Debye-like dielectric relaxation. A one-to-one correspondence to alcohols is not obvious, since H₂O's local bonding is

predominantly fourfold in character. Essentially chainlike features were nevertheless identified from molecular-dynamics simulations of water [35]. It remains to be seen how the cohesive forces arise which seem necessary to support the persistence of chainlike structures in water.

In summary, NMR measurements were exploited to derive a transient-chain model for which the average number N of temporarily H-bonded molecules could be determined. The experimental $\tau_{\text{OH}}/\tau_{\alpha}$ and $\Delta\varepsilon_{\text{D}}/\Delta\varepsilon_{\alpha}$ ratios consistently gave $N = 5\text{--}10$. Furthermore, the model predicts that the hydrodynamic radius of the diffusing species is of the size of a single alcohol molecule, which was quantitatively confirmed experimentally. Taken together, the current model rationalizes *all* so-far puzzling features associated with the Debye process in monohydroxy alcohols.

We thank A. Geiger and H. Weingärtner for stimulating discussions and A. Nowaczyk for helping with Fig. 4. Support of this project by the Deutsche Forschungsgemeinschaft under Grant No. BO1301/8-1 is gratefully acknowledged.

*catalin.gainaru@tu-dortmund.de

†roland.bohmer@tu-dortmund.de

- [1] P. Debye, *Polare Molekeln* (Hirzel, Leipzig, 1929).
- [2] D. W. Davidson and R. H. Cole, *J. Chem. Phys.* **19**, 1484 (1951).
- [3] S. K. Garg and C. P. Smyth, *J. Phys. Chem.* **69**, 1294 (1965).
- [4] C. Hansen, F. Stickel, T. Berger, R. Richert, and E. W. Fischer, *J. Chem. Phys.* **107**, 1086 (1997).
- [5] M. Tomsic, A. Jamnik, G. Fritz-Popovski, O. Glatter, and L. Vlcek, *J. Phys. Chem. B* **111**, 1738 (2007).
- [6] V. V. Levin and Y. D. Feldman, *Chem. Phys. Lett.* **87**, 162 (1982); G. Oster and J. G. Kirkwood, *J. Chem. Phys.* **11**, 175 (1943).
- [7] The occurrence of rings or micelles was also discussed; see, e.g., M. A. Floriano and C. A. Angell, *J. Chem. Phys.* **91**, 2537 (1989).
- [8] W. Dannhauser and R. H. Cole, *J. Chem. Phys.* **23**, 1762 (1955).
- [9] K. S. Vahvaselkä, R. Serimaa, and M. Torkkeli, *J. Appl. Crystallogr.* **28**, 189 (1995); L. Zoranik, F. Sokolic, and A. Perera, *J. Chem. Phys.* **127**, 024502 (2007).
- [10] J. L. MacCallum and D. P. Tieleman, *J. Am. Chem. Soc.* **124**, 15085 (2002).
- [11] J. Lehtola, M. Hakala, and K. Hämäläinen, *J. Phys. Chem. B* **114**, 6426 (2010).
- [12] H. Huth, L.-M. Wang, C. Schick, and R. Richert, *J. Chem. Phys.* **126**, 104503 (2007).
- [13] B. Jakobsen, C. Maggi, T. Christensen, and J. C. Dyre, *J. Chem. Phys.* **129**, 184502 (2008).
- [14] See, e.g., U. Kaatze, R. Behrends, and R. Pottel, *J. Non-Cryst. Solids* **305**, 19 (2002).
- [15] T. El Goresy and R. Böhmer, *J. Chem. Phys.* **128**, 154520 (2008), and references therein.
- [16] M. Pöschl and H. G. Hertz, *J. Phys. Chem.* **98**, 8195 (1994); T. Frech and H. G. Hertz, *Ber. Bunsen-Ges. Phys. Chem.* **89**, 948 (1985); M. Butsch and H. Sillescu (unpublished) provide T_1 data on propanol aiming at mapping out intramolecular flexibilities.
- [17] The ^1H and ^2H alkyl data in Fig. 1 involve methyl group contributions hampering a precise evaluation of τ_{alkyl} .
- [18] For details regarding experiments and data treatment, see R. Meier, R. Kahlau, D. Kruk, and E. A. Rössler, *J. Phys. Chem. A* **114**, 7847 (2010).
- [19] H. Nadolny, A. Volmari, and H. Weingärtner, *Ber. Bunsen-Ges. Phys. Chem.* **102**, 866 (1998).
- [20] Their magnetic dipole interaction is ~ 6.5 times stronger than the ^1H - ^2H coupling and the still weaker magnetic interactions with other molecules.
- [21] C. Lederle, W. Hiller, C. Gainaru, and R. Böhmer (to be published).
- [22] A. Anson, R. Garriga, S. Martínez, P. Pérez, and M. Gracia, *J. Chem. Eng. Data* **50**, 1478 (2005).
- [23] J. T. Edward, *J. Chem. Educ.* **47**, 261 (1970).
- [24] G. Strobl, *The Physics of Polymers* (Springer, Berlin, 1997).
- [25] N. P. Franks, M. H. Abraham, and W. R. Lieb, *J. Pharm. Sci.* **82**, 466 (1993).
- [26] L.-M. Wang and R. Richert, *J. Chem. Phys.* **121**, 11170 (2004).
- [27] At $T = 140$ K the strength of the Debye peak $\Delta\varepsilon_{\text{D}}$ of butanol is ~ 7 times larger than estimated from its dipole moment $\mu = 1.66$ D [15], and its $\Delta\varepsilon_{\alpha}$ is ~ 4 times smaller than estimated from μ .
- [28] C. P. Smyth, *Dielectric Behavior and Structure* (McGraw-Hill, New York, 1955), p. 244.
- [29] O. E. Kalinovskaya and J. K. Vij, *J. Chem. Phys.* **112**, 3262 (2000); S. S. N. Murthy and M. Tyagi, *J. Chem. Phys.* **117**, 3837 (2002); L.-M. Wang and R. Richert, *J. Phys. Chem. B* **109**, 8767 (2005).
- [30] D. Fragiadakis, C. M. Roland, and R. Casalini, *J. Chem. Phys.* **132**, 144505 (2010).
- [31] A. Reiser, G. Kasper, C. Gainaru, and R. Böhmer, *J. Chem. Phys.* **132**, 181101 (2010).
- [32] This is not obvious from recent data, see L. M. Wang, Y. Tian, R. Liu, and R. Richert, *J. Chem. Phys.* **128**, 084503 (2008), but also not incompatible with inverse calorimetry work, see W. Huang and R. Richert, *J. Chem. Phys.* **130**, 194509 (2009).
- [33] M. Maroncelli and G. R. Fleming, *J. Chem. Phys.* **86**, 6221 (1987); H. Wendt and R. Richert, *J. Phys. Chem. A* **102**, 5775 (1998).
- [34] R. Coelho and D. K. Manh, *C.R. Acad. Sci. Paris C* **264**, 641 (1967); J. Crossley and G. Williams, *J. Chem. Soc., Faraday Trans. 2* **73**, 1906 (1977).
- [35] Simulations of water reveal chainlike structures; see Fig. 10 in A. Geiger, M. Kleene, D. Paschek, and A. Rehtanz, *J. Mol. Liq.* **106**, 131 (2003); A. Geiger (private communication); N. Giovambattista, S. V. Buldyrev, F. W. Starr, and H. E. Stanley, *Phys. Rev. Lett.* **90**, 085506 (2003).