Communication: Linking the dielectric Debye process in mono-alcohols to density fluctuations

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This work provides the first direct evidence that the puzzling dielectric Debye process observed in mono-alcohols is coupled to density fluctuations. The results open up for an explanation of the Debye process within the framework of conventional liquid-state theory. The spectral shape of the dynamical bulk modulus of the two studied mono-alcohols, 2-ethyl-1-hexanol and 4-methyl-3-heptanol, is nearly identical to that of their corresponding shear modulus, and thus the supramolecular structures believed to be responsible for the slow dielectric Debye process are manifested in the bulk modulus *in the same way* as in the shear modulus. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4947470]

Almost all liquids can form a glass.[1–8] The most common route to the glassy state is through the supercooled liquid state where the liquid gradually becomes more and more viscous upon cooling and eventually falls out of equilibrium and forms a glass. Many viscous liquids display strikingly similar dynamical behavior regardless of their specific chemistry and this universality intrigues many physicists.[1–9] But although the field is old, the hallmark features of viscous liquids dynamics—non-Arrhenius temperature dependence of the viscosity and non-exponential relaxation—remain some of the major unsolved puzzles in condensed matter physics.

A class of liquids that do not conform to the general picture is the mono-alcohols. Mono-alcohols have become a hot topic in recent years.[10] Supercooled mono-alcohols differ from other viscous liquids in that the dominant process in the dielectric spectrum is as follows: (1) Close to single-exponential rather than following the stretched exponential form found in most viscous liquids;[11–13] Debye's model[14] for non-interacting dipoles in an external electrical field also predicts a single exponential response, and the process is therefore often referred to as the "Debye-process." (2) Not associated with the structural glass transition.[15–18] The faster process emerging on the high-frequency flank of the Debye process correlates much better with the structural glass transition and this process has accordingly been identified as the alpha process.[15,16,19] (3) Unusually intense. The Debye process is often so intense that it must originate from some structural correlation of several dipoles in the liquid. Dilution studies[20–23] and studies of structural isomers[24,25] show that these characteristics may be less distinct, when the Debye process is not well-separated from the alpha process.

The notion that this intense dielectric signal originates from linear hydrogen-bonded structures appeared quite early,[13,26–28] and observations of a pre-peak in the static structure factor for the mono-alcohol tert-butanol[29] supports this idea by identifying structures on a length scale exceeding the molecular. The different intensities of the Debye process in different mono-alcohols can be rationalized in terms of these structures being primarily chain-like—leading to a large

end-to-end dipole moment—or ring-like—resulting in a (partial) cancellation of the individual dipole moments.[13]

A number of mechanisms have been suggested to account for the slow dynamics of the Debye process: breaking of hydrogenbonds in a chain and formation of new chains leading to end-to-end fluctuations of the dipole moment,[30–32] dipole inversion by rotation of the OH-groups,[33] and the transient chain model advocated by Gainaru,[34] where molecules break off from or add to the ends of the chain promoting a slow rotation of the effective dipole moment of the chain. A fundamental and predictive model for the elusive Debye process is however still lacking. In particular, these proposed underlying mechanisms have little to say about whether or not this intense dielectric signal should be manifested in other types of responses. For years the consensus was that the Debye process is not linked to the mechanical or calorimetric responses, as summarized in 1997 by Hansen *et al.* that the Debye process "possesses no counterpart signals in the quantities directly related to structural relaxation like viscosity and density fluctuations."[16] Earlier shear modulus measurements seemed to confirm this picture.[19] However, there were some indications of a mechanical signature of the Debye process in ultrasonic measurements,[31,35] and it was recently established that the Debye process indeed has a weak shear mechanical counterpart.[36] The rheological response is similar to what is observed for short-chain polymers.[25,36–38]

A natural next step is to look for signatures in other relevant response functions. Could the dielectric Debye process in fact be coupled to the density fluctuations? This would open up a new route for modeling the Debye process. Density and density fluctuations are the central concepts in liquid state theory, where they define standard hydrodynamics,[39] mode-coupling theory,[40–42] and general density functional theory.[43–45] Moreover, density fluctuations provide a link to classical thermodynamics, where the state variables are scalar quantities such as pressure, volume, temperature, and entropy. Both shear mechanics and dielectrics are non-scalar observables, and since a signature of the Debye process is thus far completely absent in the

144, 161103-1

standard calorimetric scans[10] and more advanced calorimetric spectroscopic methods,[18] there is no established connection to thermodynamics.

Experimentally density fluctuations may be probed by measuring the volume response to a (linear) pressure perturbation. Recently, Dzida and Kaatze[46] published a study comparing the static adiabatic compressibility and the dielectric relaxation time of a range of mono-alcohols and showed how the concentration of hydrogenbonds affects the Debye relaxation time and the static compressibility at room temperature. But from this study, no clear conclusion can be drawn about the dielectric Debye process' manifestation in the compressibility spectrum.

Here complex adiabatic bulk modulus data measured over roughly four decades in frequency over a range of temperatures close to T_g is presented. The adiabatic bulk modulus is defined as $K_S = V(\partial P/\partial V)_S$, i.e., the inverse of the compressibility. The experimental setup including custom-built cryostat and electronics is described in Refs. 47 and 48 and the bulk modulus measuring technique in Refs. 49 and 50. Further experimental details and details on the data extraction procedure can be found the supplementary material.[51]

The bulk modulus spectra of 2-ethyl-1-hexanol (2E1H) are shown in Fig. 1. The frequency range of this measurement is from 2 Hz to 10 kHz. We clearly see the low-frequency liquid-like plateau at the high temperatures (red curves) and the high-frequency elastic plateau of the lower temperatures (blue curves) in the real part (Fig. 1(a)). The transition from low- to high-frequency plateau gives a peak in the imaginary part (Fig. 1(b)) as required by the Kramers-Kronig relations. The peak is the alpha relaxation peak, which moves down in frequency from around 10 kHz at 170 K to around 10 Hz at 154 K. A master curve was constructed (shown as an inset Fig. 1(c)) by shifting each of the curves on the frequency axis to give the best overlap. The shift factors are shown in Fig. 1(c) together with the loss peak frequencies for the temperatures where the peak is inside the frequency window. There is excellent agreement between the two characteristic frequencies in the overlapping temperature region, thus confirming that the shifts made are reasonable. The temperature dependence of the shift factors has the non-Arrhenius form characteristic for most supercooled liquids. For comparison, literature values of the dielectric relaxation frequencies for alpha and Debye process[52] are included. The values were obtained as $f = (2\pi\tau)^{-1}$ and shifted by the same factor as the bulk modulus peak frequencies. The alpha frequencies from bulk modulus and dielectric spectra are not directly comparable since former comes from a peak frequency and the latter from a relaxation time of a fitted functional form, but the two are proportional within noise showing that they display the same non-Arrhenius temperature behavior.

The main example is the 2E1H, but 4-methyl-3-heptanol (4M3H) was also measured. The bulk modulus data for 4M3H are shown in Fig. 2. For this sample, it was difficult to reach temperatures closer to T_g, most likely due to a cavity forming inside the measuring cell at low temperatures causing a distortion of the signal. So in the case of 4M3H, there are no spectra showing the elastic (high-frequency) plateau in
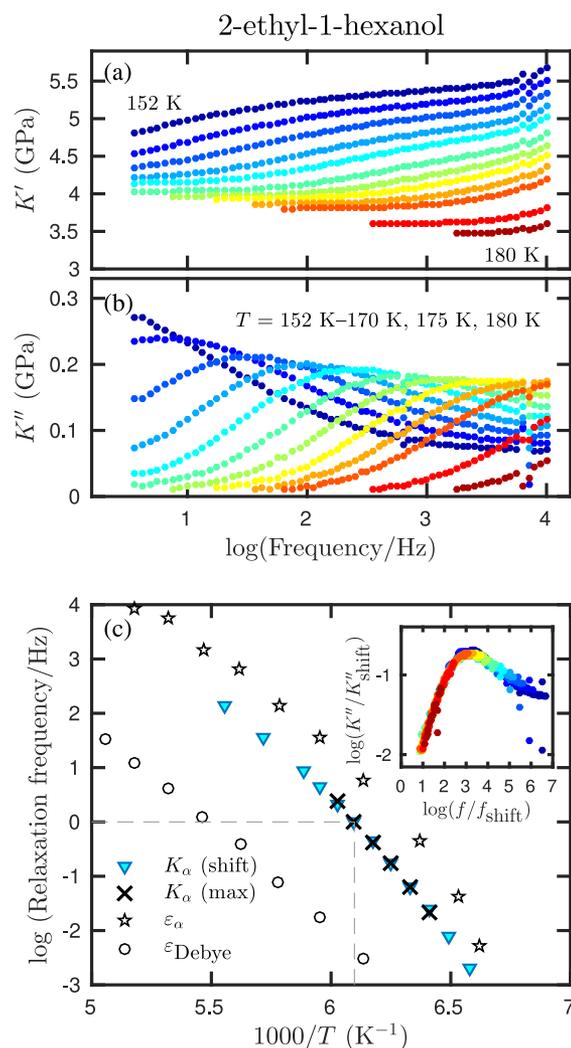

FIG. 1. Complex bulk modulus of 2E1H at several temperatures in 2 K steps from 152 K to 170 K and at 175 K and 180 K. (a) Real part of the bulk modulus. (b) Imaginary part of the bulk modulus. (c) The shift factors (obtained by constructing the master curve shown in the inset) as a function of inverse temperature. The reference (164 K) is marked by the dashed lines. For comparison, the peak frequencies (shifted to overlap at the reference temperature) are shown as well as the dielectric alpha and Debye relaxation frequency from Ref. 52 obtained as $f = (2\pi\tau)^{-1}$ and shifted with the same factor as the bulk modulus loss-peaks. The characteristic alpha frequencies of dielectric and bulk modulus spectra are proportional and thus display similar non-Arrhenius temperature dependences.

the real part. However, for the point of this paper, having a well-resolved low-frequency part of the modulus is sufficient.

Figure 3 compares the imaginary parts of bulk modulus K (blue diamonds) and shear modulus G (yellow line) at a selected temperature for both 2E1H (Fig. 3(a)) and 4M3H (Fig. 3(b)). For comparison, the dielectric curve at the same temperature (or close) is shown (red solid line). For 2E1H, the dominant feature in the dielectric spectrum is the Debye process and the alpha process is manifested as a high-frequency shoulder placed roughly where the alpha peak in the mechanical spectra appears. For 4M3H, the intensity of the dielectric Debye process is comparable to the alpha process and the two processes are less separated in frequency.

The recently established rheological signature of the Debye process[36] shows up in the shear spectra as a deviation
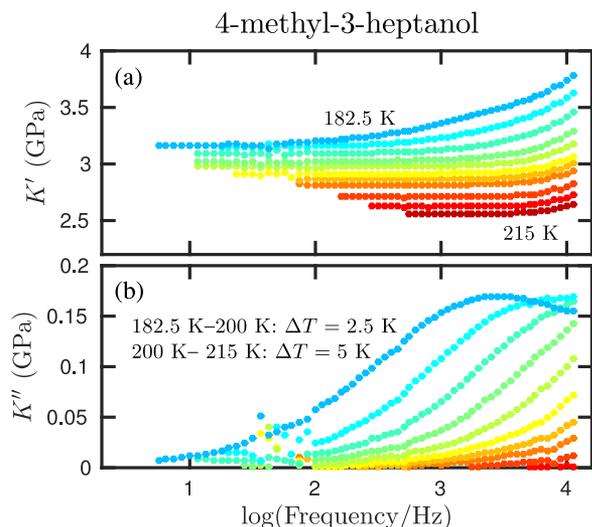
FIG. 2. Real (a) and imaginary (b) parts of the bulk modulus of 4M3H. Due to experimental difficulties, it was not possible to go closer to the glass transition temperature. However, for the purpose of this paper, a well-resolved low-frequency part of the alpha relaxation suffices.
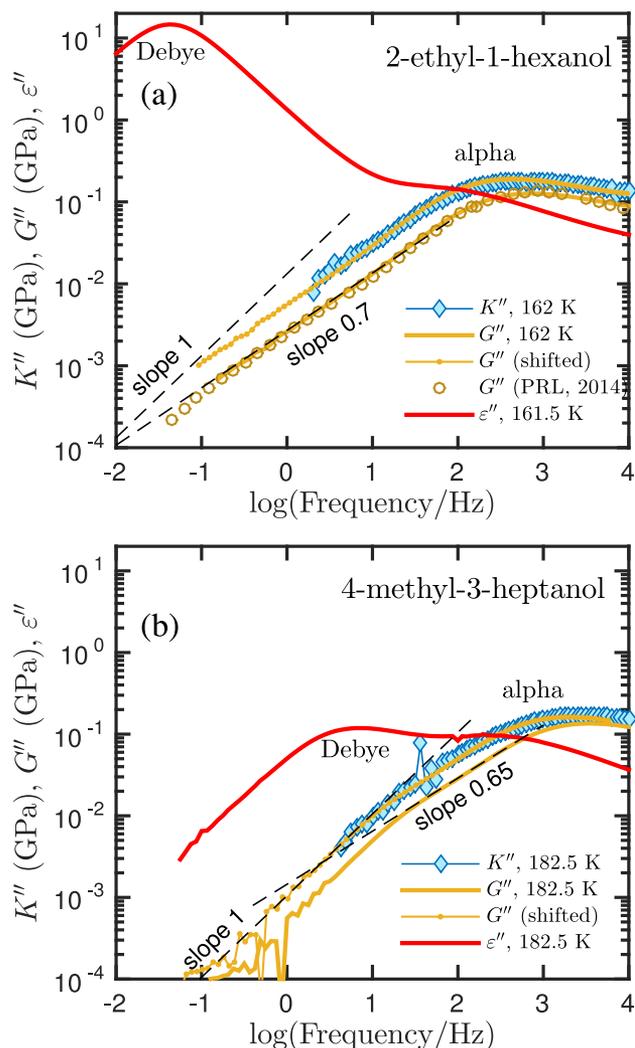

FIG. 3. Comparison of the imaginary parts of the bulk modulus (blue diamonds), shear modulus (solid yellow line), and dielectric constant (solid red line) for (a) 2E1H and (b) 4M3H at a fixed temperature. (a) The shear modulus is compared to the master curve presented in Ref. 36 (yellow circles) and reproduces the literature data. The rheological signature of the short-chain polymer-like behavior is a slope <1 on the low-frequency side of the alpha peak bending over to a purely viscous behavior (unity slope) at ∼0.1 Hz, corresponding roughly to the loss-peak frequency of the Debye peak in the dielectric spectrum. The bulk modulus curve follows the low-frequency behavior of the shear modulus accurately, which is demonstrated by shifting the shear modulus curve to overlap the bulk modulus spectrum. The crossover to purely viscous behavior in the bulk modulus is however below the resolution limit of the bulk modulus measurement. (b) In 4M3H, we again observe that the spectral anomalies of the shear modulus are repeated in the bulk modulus, only shifted to slightly lower frequencies.

from the pure viscous behavior observed for non-associated liquids characterized by $G''(\omega) \propto \omega$ (unity slope in a double-logarithmic plot). The crossover from this intermediate low-frequency power law behavior with $G''(\omega) \propto \omega^s, s < 1$ to the terminal viscous flow with $G''(\omega) \propto \omega$ behavior is located at a frequency close to the Debye peak frequency in the dielectric spectrum. For 2E1H, this means that the intermediate power law region extends over 4 decades and only the onset of the crossover to pure viscous behavior is seen in the master-curve of Ref. 36 (yellow circles). For 4M3H the intermediate power law region extends only two decades in the shear modulus (in agreement with a smaller separation between alpha and Debye process in the dielectric spectrum) and the pure viscous behavior is evident over 1-2 decades.

For both 2E1H and 4M3H, the bulk modulus relaxation is slower than the shear modulus relaxation by a factor of around two. Shifting the shear mechanical curve (yellow connected dots) gives a perfect overlap with the bulk modulus data, thus showing that the bulk modulus displays the same spectral features and evidently the same deviation from pure viscous behavior as the shear modulus. For 2E1H, the resolution of the bulk modulus measurement does not allow for showing the crossover to a pure viscous behavior. For 4M3H, the crossover should just barely be in the resolution window of the bulk modulus measurement due to the shorter separation between alpha and Debye process. Indeed, the bulk modulus curve does seem to crossover in the same way as the shear modulus curve, although the actual kink is less evident due to noise in the data. The bulk modulus of non-associated liquids typically displays a low-frequency purely viscous ($K'' \propto \omega$) behavior[50,53] at frequencies below the alpha peak; hence a terminal, pure viscous behavior is certainly expected at frequencies and moduli below our current resolution limit.

Compared to poly-alcohols, the relaxation strength of the bulk modulus (and the shear modulus) of the mono-alcohols is quite modest, around 1 GPa at the lowest temperatures. This relaxation strength is similar to what has been found for the shear modulus of other mono-alcohols, for instance, *n*-propanol,[54] 1-octanol, and 2-octanol,[55] and also what is typically found for the bulk and shear modulus of non-associated, molecular liquids.[50,53] In glycerol[56] and propylene glycol,[53,57] the relaxation strength is a factor of four higher. We speculate that this fact may be understood in terms of the type of molecular network formed in the poly-alcohols compared to the mono-alcohols. Poly-alcohols can form branched hydrogen-bonded networks which could lead to a stiffer structure and thus higher bulk and shear moduli. The mono-alcohols, on the other hand, primarily form linear structures (chains and/or rings) giving a "looser"

structure, which is easier to deform and compress. The signature of these structures in the shear spectra is a subtle deviation from pure viscous behavior on the low-frequency side of the alpha peak, similar to that of a short-chain polymer.[25,36–38] It is not trivial, however, that the bulk modulus of mono-alcohols deviates from that of non-associated liquids.

The two studied mono-alcohols represent two ends of the range of the different mono-alcohol behaviors: The dielectric Debye process in 2E1H is very intense and separated from the alpha process by 4 decades in frequency, whereas in 4M3H, the Debye process has roughly the same intensity as the alpha, and the time scales of the two processes are much closer (see Fig. 3). The rheological signature of the Debye process complies with this picture;[25,36,37] in that extent of the non-trivial power law region at frequencies below the shear modulus, alpha peak correlates with the time separation between the dielectric Debye and alpha process. The results presented here show that the bulk modulus systematically displays the same anomalous low frequency behavior as the shear modulus. Thus the dielectric Debye process observed in mono-alcohols indeed couples directly to the density fluctuations in the liquid. One such coupling between density and the Debye process naturally enters through the model picture of fluctuations between ring and chain structures (discussed in Ref. 32), which are known to have different densities,[10] but there could be other possible alternatives.

[1]W. Kauzmann, Chem. Rev. **43**, 219 (1948).

[2]G. W. Scherer, *Relaxation in Glass and Composites* (Wiley, New York, 1986).

[3]M. D. Ediger, C. A. Angell, and S. R. Nagel, J. Phys. Chem. **100**, 13200 (1996).

[4]C. A. Angell, K. L. Ngai, G. B. McKenna, P. F. McMillan, and S. W. Martin, J. Appl. Phys. **88**, 3113 (2000).

[5]P. G. Debenedetti and F. H. Stillinger, Nature **410**, 259 (2001).

[6]J. C. Dyre, Rev. Mod. Phys. **78**, 953 (2006).

[7]M. D. Ediger and P. Harrowell, J. Chem. Phys. **137**, 080901 (2012).

[8]L. Berthier and M. Ediger, Phys. Today **69**(1), 40 (2016).

[9]J. P. Garrahan and D. Chandler, Proc. Natl. Acad. Sci. U. S. A. **100**, 9710 (2003).

[10]R. Böhmer, C. Gainaru, and R. Richert, Phys. Rep. **545**, 125 (2014).

[11]D. W. Davidson and R. H. Cole, J. Chem. Phys. **19**, 1484 (1951).

[12]R. H. Cole and D. W. Davidson, J. Chem. Phys. **20**, 1389 (1952).

[13]W. Dannhauser, J. Chem. Phys. **48**, 1911 (1968).

[14]P. Debye, *Polar Liquids* (The Chemical Catalog Company, Inc., New York, 1929).

[15]A. Kudlik, C. Tschirwitz, S. Benkhof, T. Blochowicz, and E. Rössler, Europhys. Lett. **40**, 649 (1997).

[16]C. Hansen, F. Stickel, T. Berger, R. Richert, and E. W. Fischer, J. Chem. Phys. **107**, 1086 (1997).

[17]L. M. Wang and R. Richert, J. Chem. Phys. **121**(22), 11170 (2004).

[18]H. Huth, L.-M. Wang, C. Schick, and R. Richert, J. Chem. Phys. **126**, 104503 (2007).

[19]B. Jakobsen, C. Maggi, T. Christensen, and J. C. Dyre, J. Chem. Phys. **129**, 184502 (2008).

[20]S. Schwerdtfeger, F. Köhler, R. Pottel, and U. Kaatze, J. Chem. Phys. **115**, 4186 (2001).

[21]M. Preuss, C. Gainaru, T. Hecksher, S. Bauer, J. C. Dyre, R. Richert, and R. Böhmer, J. Chem. Phys. **137**, 144502 (2012).

[22]S. Bauer, H. Wittkamp, S. Schildmann, M. Frey, W. Hiller, T. Hecksher, N. B. Olsen, C. Gainaru, and R. Böhmer, J. Chem. Phys. **139**, 134503 (2013).

[23]Y. Gao, W. Tu, Z. Chen, Y. Tian, R. Liu, and L.-M. Wang, J. Chem. Phys. **139**, 164504 (2013).

[24]S. S. N. Murthy, J. Phys. Chem. **100**, 8508 (1996).

[25]T. Hecksher and B. Jakobsen, J. Chem. Phys. **141**, 101104 (2014).

[26]G. P. Johari and W. Dannhauser, J. Phys. Chem. **72**, 3273 (1968).

[27]M. A. Floriano and C. A. Angell, J. Chem. Phys. **91**, 2537 (1989).

[28]M. Iwahashi, Y. Hayashi, N. Hachiya, H. Matsuzawa, and H. Kobayashi, J. Chem. Soc. Faraday Trans. **89**, 707 (1993).

[29]D. Morineau and C. Alba-Simionesco, J. Phys. Chem. Lett. **1**, 1155 (2010).

[30]O. E. Kalinovskaya and J. K. Vij, J. Chem. Phys. **112**, 3262 (2000).

[31]U. Kaatze, R. Behrends, and R. Pottel, J. Non-Cryst. Solids **305**, 19 (2002).

[32]L. P. Singh and R. Richert, Phys. Rev. Lett. **109**, 167802 (2012).

[33]R. Minami, K. Itoh, H. Takahashi, and K. Higasi, J. Chem. Phys. **73**, 3396 (1980).

[34]C. Gainaru, R. Meier, S. Schildmann, C. Lederle, W. Hiller, E. A. Rössler, and R. Böhmer, Phys. Rev. Lett. **105**, 258303 (2010).

[35]R. Behrends and U. Kaatze, J. Phys. Chem. A **105**, 5829 (2001).

[36]C. Gainaru, R. Figuli, T. Hecksher, B. Jakobsen, J. C. Dyre, M. Wilhelm, and Böhmer, Phys. Rev. Lett. **112**, 098301 (2014).

[37]C. Gainaru, M. Wikarek, S. Pawlus, M. Paluch, R. Figuli, M. Wilhelm, T. Hecksher, B. Jakobsen, J. C. Dyre, and R. Böhmer, Colloid Polym. Sci. **292**, 1913 (2014).

[38]K. Adrjanowicz, B. Jakobsen, T. Hecksher, K. Kaminski, M. Dulski, M. Paluch, and K. Niss, J. Chem. Phys. **143**, 181102 (2015).

[39]J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 4th ed. (Elsevier, 2013).

[40]J. Bosse, W. Götze, and M. Lücke, Phys. Rev. A **17**, 434 (1978).

[41]W. Götze and L. Sjögren, Rep. Prog. Phys. **55**, 241 (1992).

[42]S. P. Das, Rev. Mod. Phys. **76**, 785 (2004).

[43]R. Evans, Adv. Phys. **28**, 143 (1979).

[44]Y. Rosenfeld, Phys. Rev. Lett. **63**, 980 (1989).

[45]R. Evans, "Density functionals in the theory of nonuniform fluids," in *Fundamentals of Inhomogeneous Fluids* (Marcel Dekker, 1992), pp. 85–176.

[46]M. Dzida and U. Kaatze, J. Phys. Chem. B **119**, 12480 (2015).

[47]B. Igarashi, T. Christensen, E. H. Larsen, N. B. Olsen, I. H. Pedersen, T. Rasmussen, and J. C. Dyre, Rev. Sci. Instrum. **79**, 045105 (2008).

[48]B. Igarashi, T. Christensen, E. H. Larsen, N. B. Olsen, I. H. Pedersen, T. Rasmussen, and J. C. Dyre, Rev. Sci. Instrum. **79**, 045106 (2008).

[49]T. Christensen and N. B. Olsen, Phys. Rev. B **49**, 15396 (1994).

[50]T. Hecksher, N. B. Olsen, K. A. Nelson, J. C. Dyre, and T. Christensen, J. Chem. Phys. **138**, 12A543 (2013).

[51]See supplementary material at http://dx.doi.org/10.1063/1.4947470 for details on experiments and data analysis.

[52]C. Gainaru, S. Kastner, F. Mayr, P. Lunkenheimer, S. Schildmann, H. J. Weber, W. Hiller, A. Loidl, and R. Böhmer, Phys. Rev. Lett. **107**, 118304 (2011).

[53]D. Gundermann, K. Niss, T. Christensen, J. C. Dyre, and T. Hecksher, J. Chem. Phys. **140**, 244508 (2014).

[54]R. Kono, T. A. Litovitz, and G. E. McDuffe, J. Chem. Phys. **45**, 1790 (1966).

[55]F. Palombo, P. Sassi, M. Paolantoni, A. Morresi, and R. S. Cataliotti, J. Phys. Chem. B **110**, 18017 (2006).

[56]C. Klieber, T. Hecksher, T. Pezeril, D. H. Torchinsky, J. C. Dyre, and K. A. Nelson, J. Chem. Phys. **138**, 12A544 (2013).

[57]C. Maggi, B. Jakobsen, T. Christensen, N. B. Olsen, and J. C. Dyre, J. Phys. Chem. B **112**, 16320 (2008).