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Communication: Identical temperature dependence of the time scales of several linear-response functions of two glass-forming liquids

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The frequency-dependent dielectric constant, shear and adiabatic bulk moduli, longitudinal thermal expansion coefficient, and longitudinal specific heat have been measured for two van der Waals glass-forming liquids, tetramethyl-tetraphenyl-trisiloxane (DC704) and 5-polyphenyl-4-ether. Within the experimental uncertainties the loss-peak frequencies of the measured response functions have identical temperature dependence over a range of temperatures, for which the Maxwell relaxation time varies more than nine orders of magnitude. The time scales are ordered from fastest to slowest as follows: Shear modulus, adiabatic bulk modulus, dielectric constant, longitudinal thermal expansion coefficient, and longitudinal specific heat. The ordering is discussed in light of the recent conjecture that van der Waals liquids are strongly correlating, i.e., approximate single-parameter liquids. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3690083]

A liquid has several characteristic times.[1–4] One is the Maxwell relaxation time determining how fast stress relaxes $\tau_M \equiv \eta/G_\infty$, where η is the shear viscosity and G_∞ the instantaneous shear modulus.[5] Other characteristic times are identified by writing $D = a^2/\tau_D$, in which D may be particle, heat, or the transverse momentum diffusion constant, and a is the intermolecular distance. Further characteristic times are the inverse loss-peak frequencies (i.e., frequencies of maximum imaginary part) of different complex frequency-dependent linear-response functions.[6,7] For low-viscosity liquids like ambient water the characteristic times are all of the same order of magnitude, in the picosecond range, and only weakly dependent on temperature.

Supercooling a liquid increases dramatically its viscosity;[8–12] most characteristic times likewise increase dramatically. The metastable equilibrium liquid can be cooled until the relaxation times become of order 10^{15} times larger than for the low-viscosity liquid, at which point the system falls out of metastable equilibrium and forms a glass. At typical laboratory cooling rates (K/min) the glass transition takes place when τ_M is of order 100 s.[8–12]

Even though most characteristic times increase dramatically when the liquid is cooled, they are generally not identical. Different measured quantities and different definitions of the characteristic time scale lead to different characteristic times. A trivial example is the difference between the time scales of the bulk modulus and its inverse in the frequency domain, the bulk compressibility. More interestingly, some time scales might have quite different temperature dependence; this is often referred to as a *decoupling* of the corresponding microscopic processes.

Several relaxation time decouplings have been reported in the ultraviscous liquid state above the glass transition. Significant decoupling takes place for some glass-forming molten salts like "CKN" (a 60/40 mixture of $Ca(NO_3)_2$ and KNO_3 (Ref. 13)), where the conductivity relaxation time at the glass transition is roughly 10^4-10^5 times smaller than τ_M.[14,15] This reflects a decoupling of the molecular motions, with the cations diffusing much faster than the nitrate ions.[15] A more recent discovery is the decoupling of translational and rotational motion in most molecular liquids, for which one often finds that molecular rotations are 10–100 times slower than expected from the diffusion time.[16–18] This is generally believed to reflect dynamic heterogeneity of glass-forming liquids.[16–19] Angell in 1991 suggested a scenario consisting of "a series of decouplings which occurs on decreasing temperature", sort of a hierarchy. He cautiously added, though, that "more data are urgently needed to decide if this represents the general case".[15]

Some linear-response functions like the thermoviscoelastic and shear-mechanical ones are difficult to measure reliably for ultraviscous liquids.[20–22] To the best of our knowledge there are no studies of their possible decoupling. This paper presents such data, together with conventional dielectric data. The purpose is to establish the order of relaxation times among the different quantities and, in particular, to investigate whether or not they show a decoupling upon approaching the glass-transition temperature.

I. EXPERIMENTAL RESULTS

We have measured the complex, frequency-dependent dielectric constant $\varepsilon(\omega)$, shear modulus $G(\omega)$,[20,23] adiabatic bulk modulus $K_S(\omega)$,[23,24] and longitudinal specific heat $c_l(\omega)$ (Ref. 25) on the two van der Waals bonded glass-forming liquids tetramethyl-tetraphenyl-trisiloxane (DC704) and 5-polyphenyl-4-ether (5PPE) (commercial vacuum-pump oils). For DC704, the time-dependent longitudinal thermal expansion coefficient $\alpha_l(t)$ (Ref. 26) was also measured (see

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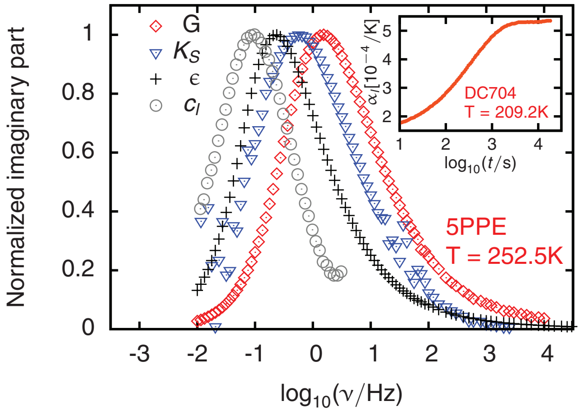

FIG. 1. Example of data from which loss-peak positions are found. Main part: Normalized imaginary parts of the following complex response functions: shear modulus $G(\omega)$, adiabatic bulk modulus $K_S(\omega)$, dielectric constant $\epsilon(\omega)$, and longitudinal specific heat $c_l(\omega)$, as functions of frequency for 5-polyphenyl-4-ether (5PPE) at $T = 252.5$ K. Inset: Time-dependent longitudinal expansion coefficient $\alpha_l(t)$ at $T = 209.2$ K for tetramethyl-tetraphenyl-trisiloxane (DC704), measured by a technique which is not applicable to 5PPE.

supplementary material[27] for details). We note that both liquids have linear-response functions that to a good approximation obey time-temperature superposition (TTS),[23,28,29] i.e., their loss-peak shapes are temperature independent in log-log plots. Moreover, the two liquids have only small beta relaxations, they rarely crystallize, and they are generally very stable and reproducible—altogether these two liquids are very suitable for fundamental studies.

Three of the measured quantities (α_l, c_l, and K_S) are closely related to one complete set of independent scalar thermoviscoelastic response functions:[30,48] c_p, α_p, and κ_T (the relations are given in the supplementary material[27]). Measurements of such a complete set of three scalar thermoviscoelastic response functions are rare, if at all existing for any glass-forming liquid.

Figure 1 shows the normalized loss peaks as functions of frequency of $G(\omega)$, $K_S(\omega)$, $\epsilon(\omega)$, and $c_l(\omega)$ for 5PPE at 252.5 K. The inset shows data for the time-dependent $\alpha_l(t)$ at $T = 209.2$ K for DC704. The frequency-domain data allow for direct determination of the loss-peak frequencies (ν_{lp}); the time-domain data were Laplace transformed to give an equivalent loss-peak frequency.[26]

The measurements give both real and imaginary parts of the complex response functions, allowing us to calculate two other relevant characteristic frequencies, namely the inverse Maxwell time $1/(2\pi\tau_M)$ (η and G_∞ can be found from $G(\omega)$) and the loss-peak frequency of the adiabatic compressibility $\kappa_S(\omega) = 1/K_S(\omega)$. Figure 2(a) shows the temperature dependence of the seven characteristic frequencies for DC704.[31] The data cover more than nine decades in relaxation time (from T_g and up). Clearly, the time scales for the response functions follow each other closely.

Figure 2(b) plots the characteristic frequencies in terms of a *"time-scale index"* defined as the logarithmic distance to the dielectric loss-peak frequency.[33] For both liquids the time-scale indices are temperature independent within the experimental uncertainty, that is, the characteristic time scales of the measured quantities change in the same way with temperature.

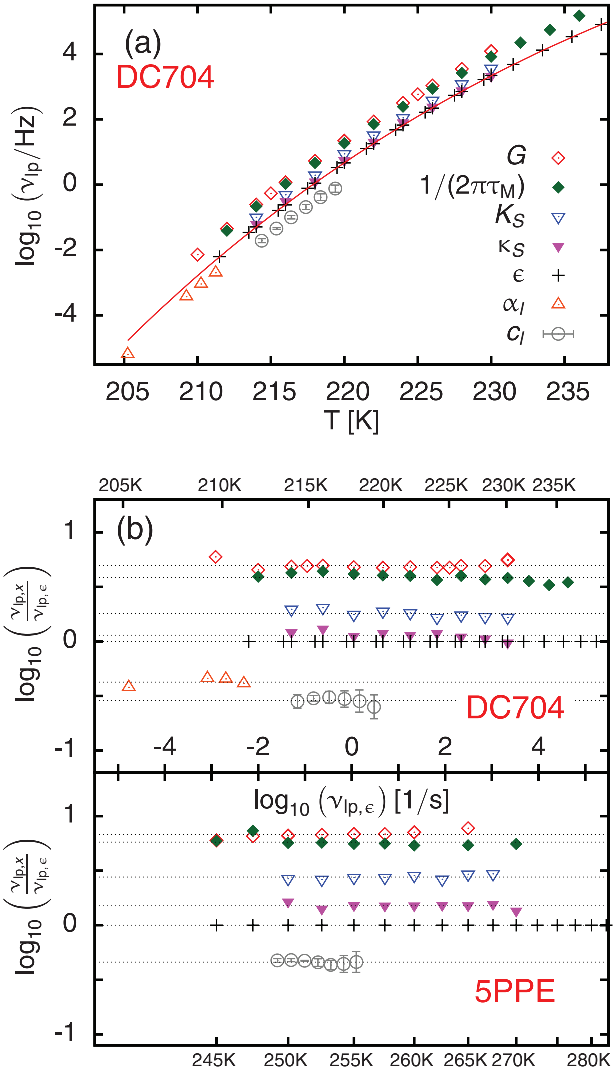

FIG. 2. (a) Seven characteristic frequencies (based on five measured quantities) as functions of temperature for DC704. The full curve is a fit of the dielectric data to a parabolic function[32] (see supplementary material[27] for details on this function), used for extrapolation of the dielectric data to low temperatures. Filled symbols (τ_M and κ_S) indicate a quantity that is not measured directly but derived from one of the measured quantities. Error bars on c_l data were estimated by assuming an additive influence from the underlying spurious frequency dependence of the raw data,[25] varying its influence on the loss peak from negligible to maximal. Equivalent data are given for 5PPE in the supplementary material.[27] (b) Time-scale index of all measured response functions (symbols as in the top figure) with respect to the dielectric constant for the two liquids DC704 and 5PPE. The time-scale index is plotted as function of the dielectric loss-peak frequency (common x-axis), which represents the temperature (also given for each liquid). For both liquids the time-scale index for all quantities are temperature independent within the experimental uncertainty, that is, the measured quantities have the same temperature dependence of their characteristic time scales.

This finding constitutes the main result of the present paper, showing that the time scales for these response functions are strongly coupled, in contrast to the observed decoupling between translational diffusion and rotation[16–18] and at variance with the scenario suggested by Angell.[15]

II. DISCUSSION

The fastest response function is the shear modulus. It has previously been reported that this quantity is faster than dielectric relaxation for a number of glass-forming liquids (see e.g., Refs. 29 and 34 and references therein), a fact that the Gemant-DiMarzio-Bishop model explains qualitatively.[35] The dielectric relaxation is faster than the specific heat (this difference cannot be attributed to measuring c_l and not c_p (Ref. 27)). For glycerol the same tendency has been reported[36,37] but with a fairly small difference in time scales of c_p and ϵ ($\approx$0.2 decades). However, a consistent interpretation of dielectric hole-burning experiments on glycerol was arrived at by assuming that these two time scales coincide.[38] For propylene glycol the opposite trend has been reported.[36] Regarding volume and enthalpy relaxation there is likewise no general trend in the literature; some glassformers have slower enthalpy than volume relaxation, others the opposite.[39–41] Clearly, more work is needed to identify any possible general trends. However, such comparisons are generally difficult, as it requires a precision in absolute temperature at least better than 1 K between the experiments. This is very difficult to obtain, and it could be speculated that some of the contradicting results could be explained this way. In our experiments all quantities except the longitudinal thermal expansion coefficient were measured in the same cryostat (for technical details see the supplementary material[27]).

What does theory have to say about the decoupling among relaxation functions and why some are faster than others? As mentioned, there are three independent scalar thermoviscoelastic response functions. There is no *a priori* reason these should have even comparable loss-peak frequencies. Moreover, both the dielectric constant and the shear modulus are linear-response functions that do not belong to the class of scalar thermoviscoelastic response functions; these two functions could in principle have relaxation times entirely unrelated to those of the scalar thermoviscoelastic response functions. All in all, general theory does not explain our findings.

As mentioned earlier, the two investigated liquids obey TTS to a good approximation and have very small (if existing) beta relaxations. In an earlier work,[29] some of us noticed that the time-scale index between shear mechanical and dielectric relaxation is only significantly temperature dependent for systems with a significant beta relaxation. In Ref. 42, it was shown for a number of systems (including systems with a pronounced beta relaxation) that the dielectric relaxation and the aging rate after a temperature jump follow the same *"inner clock"*; these results were obtained at temperatures where the alpha and beta relaxations are well separated. Based on this, one might speculate that some (or all) of the temperature dependencies of the time-scale index reported in the literature could be due to the difference in the influence from the beta relaxation between the measured response functions (see e.g., Ref. 43 for a comparison of the influence in shear mechanical and dielectric relaxation).

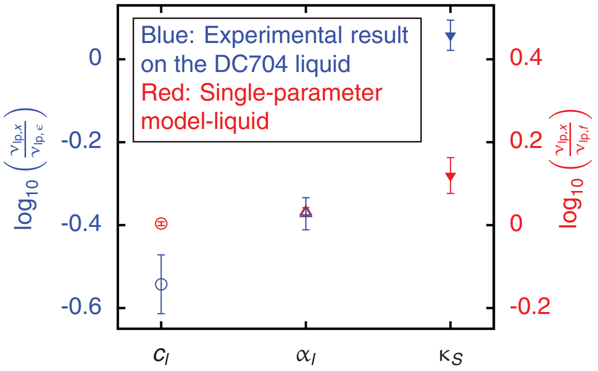

FIG. 3. Time-scale indices of c_l, α_l, and κ_S for DC704 (blue symbols, left y-axis) and for the single-parameter model-liquid (red symbols, right y-axis) (see supplementary material[27] for details on the model calculation). The two axis have been shifted with respect to each other to give an overall best overlap of the indices. For the experimental data the time-scale index is given relative to the dielectric loss-peak frequency ($\nu_{\mathrm{lp},\epsilon}$). The reported quantity is the mean over the index in Fig. 2(b), the error is based on the standard deviation (in the case of c_l a mean over maximum and minimum based on the error bars on the loss-peak frequency was used). For the single-parameter model-liquid the index is with respect to the common loss-peak frequency of α_p, c_p, and κ_T ($\nu_{\mathrm{lp},f}$). The model liquid has the same order of the time scales as the real liquid, but the differences in the time scales are underestimated in the model.

A. Comparison to a "perfectly correlating liquid"

The class of so-called "strongly correlating" liquids was recently identified.[44] This class includes most or all van der Waals and metallic liquids but not the covalently-bonded, hydrogen-bonded, or ionic liquids. In computer simulations strongly correlating liquids are characterized by strong correlations between constant-volume equilibrium fluctuations of virial and potential energy.[44] These liquids are approximate single-parameter liquids, i.e., they do not have three independent isotropic scalar thermoviscoelastic response functions but to a good approximation merely one.[45] A perfect single-parameter liquid obeys[46]

$$\frac{T_0\alpha_p''(\omega)}{c_p''(\omega)} = \gamma_{Tp} = \frac{\kappa_T''(\omega)}{\alpha_p''(\omega)}, \tag{1}$$

where γ_{Tp} is a constant. Experimental evidence that DC704 is a strongly correlating liquid, was very recently presented in Ref. 47.

We tested how well our results conform to the predictions for a perfectly correlating liquid. If thermoviscoelastic response functions obey Eq. (1), their loss-peak frequencies should be identical at all temperatures. A single-parameter model liquid was constructed by assuming Eq. (1) to hold, with high-frequency limits and relaxation strengths of the quantities chosen to be as close as possible to those measured for DC704. The quantities $\alpha_l(\omega)$, $c_l(\omega)$, and $\kappa_S(\omega)$ were calculated in the model (see supplementary material[27] for details).

Figure 3 compares the characteristic frequencies of c_l, α_l, and κ_S of our experiments to those of the model liquid. The order of the time scales for the model liquid matches the observations, i.e., c_l slower than α_l and κ_S faster than α_l. However, the magnitude of the time-scale differences is significantly underestimated.

III. SUMMARY

We measured several complex frequency-dependent linear-response functions on the two van der Waals liquids DC704 and 5PPE. Within the experimental uncertainties the time scales of the response functions have the same temperature dependence, that is, the *time-scale indices* are temperature independent. The time scales are for both liquids ordered from fastest to slowest as follows: Shear modulus, adiabatic bulk modulus, dielectric constant, longitudinal thermal expansion coefficient, and longitudinal specific heat.

General theory does not explain why the time scales of some response functions couple very closely to each other, as is the case for the investigated response functions, and why others show a decoupling, e.g., between translational diffusion and rotation.[16–18] The ordering of the longitudinal thermal expansion coefficient, the longitudinal specific heat, and the adiabatic compressibility can be rationalized by assuming that the liquids are strongly correlating, i.e., approximate single-parameter liquids.[44,46]

More work is indeed needed to establish if our findings are general for van der Waals liquids, and to understand which response functions have temperature-independent time scale index and which decouple.

ACKNOWLEDGMENTS

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[30] There are 24 different complex, frequency-dependent scalar thermoviscoelastic response functions referring to isotropic experimental conditions (see also Ref. 48). Any such linear-response function may be written as $\partial a(\omega)/\partial b(\omega)_c$ where $a, b, c \in \{T, S, p, V\}$, where T is temperature, S entropy, p pressure, and V volume. The 24 linear-response functions are not independent. A number of sets of three independent functions can be selected (e.g. c_p, α_p and κ_T), where all the remaining functions can be expressed via the generalized Onsager and standard thermodynamic relations (see also Refs. 45 and 48).
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