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# Probing heterogeneous thermal relaxation by nonlinear dielectric spectroscopy

Susan Weinstein and Ranko Richert

Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604, USA

E-mail: [richert@asu.edu](mailto:richert@asu.edu)

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## Abstract

The application of time-dependent electric fields to a sample that exhibits dielectric loss results in the irreversible transfer of energy from the external field to the slow degrees of freedom in the material. These slow modes are coupled only weakly to the phonon bath and elevated fictive temperatures are thus associated with considerable persistence times. Assuming locally correlated heterogeneities regarding dielectric and thermal relaxation times, extremely pronounced nonlinear dielectric effects are predicted. For two glass-forming systems, glycerol and propylene glycol, the predicted effects are observed experimentally by high-field impedance spectroscopy. At fields of  $283 \text{ kV cm}^{-1}$ , the dielectric loss increases by up to 9% over its low-field value. This nonlinearity displays a characteristic frequency dependence, with the loss at frequencies below the peak value being field invariant, whereas the high-frequency wing experiences a near uniform relative increase of the loss. If the dielectric and thermal time constants are assumed to be independently distributed, the model fails to explain the findings.

## 1. Introduction

Liquids, supercooled liquids, and glasses are disordered materials and thus subject to relaxation time dispersions, observed as non-exponential correlation functions [1, 2]. Such dispersive processes are associated with heterogeneous dynamics, which implies the picture of spatially varying relaxation time constants. These dynamically distinct domains are being associated with spatial dimensions of several nanometres. This heterogeneous nature of the dynamics has been assessed using numerous techniques: nuclear magnetic resonance [3], deep photobleaching [4], dielectric hole-burning [5–7], solvation dynamics [8], and computer experiments [9]. Most of these experiments have been performed in the regime of slow relaxation dynamics near the glass transition temperature  $T_g$  [10]. In this highly viscous state, relaxation time dispersions are more pronounced than at elevated temperatures [11]. It is

natural that these heterogeneities in supercooled liquids have been discovered in terms of the relaxation time constants, because this quantity is more sensitive to environmental changes than any other experimental observables such as density or local structure. Because the majority of observations concerning heterogeneity refer to the time scale of some molecular motion, less information is available regarding the spatial nature of other more thermodynamic quantities such as dynamic heat capacity or enthalpy relaxation. It is well established that both structural and thermodynamic variables display dispersive relaxation patterns [12, 13], and it is therefore interesting to explore the extent to which these features are locally correlated.

In a typical relaxation experiment, the applied external fields are small and well within the regime of linear responses. In this linear regime, two time correlation functions will not provide insight into the heterogeneous aspects of dynamics [14]. With respect to dielectric relaxation spectroscopy, nonlinear effects have been studied as well, either by large time-dependent fields or by a large bias plus a small oscillating or step field. Dielectric saturation or Langevin effects or field-induced chemical changes are usually being considered as the main sources of higher-order susceptibilities in simple liquids [15]. On the other hand, dielectric hole-burning (DHB) is a nonlinear (and non-resonant) method for studying spectral selectivity that exploits the effects of energy absorbed from the large external time-dependent electric field [5, 7, 16–19]. Apart from the interpretation and modelling of DHB and related experiments, the absorption of energy by the slow degrees of freedom is usually disregarded as a source of nonlinear dielectric effects.

In this work, we explore further the changes in the dielectric susceptibilities based solely on the slow degrees of freedom absorbing energy from the high-amplitude external field in a plain frequency domain impedance measurement [20]. The model employed to rationalize the experimental findings is based upon the dispersive nature of the frequency-dependent heat capacity, which allows translation of the absorbed energy into an increased fictive temperature  $T_f$ , which in turn decreases the relaxation time  $\tau$  according to the apparent activation energy,  $\partial \ln \tau / \partial (1/T)$ . For viscous glycerol and propylene glycol, significant increases of the dielectric loss of up to 9% are observed for electric fields as high as  $283 \text{ kV cm}^{-1}$ . The frequency dependence of this effect is very characteristic: the high-frequency wing displays a uniform relative increase of the dielectric loss, whereas the spectrum at frequencies below the peak position is not sensitive to this energy absorption effect. The findings suggest that structural and thermodynamic relaxation times are both heterogeneous *and* locally correlated quantities, as assumed for rationalizing DHB results [5–7, 16–20]. The present results demonstrate that the slow degrees of freedom are associated with heterogeneous thermal conductivities which are much below the phonon counterpart values. The phenomenological model is capable of capturing the findings quantitatively without adjustable parameters.

## 2. Model

The main goal of the model described here is to identify the nonlinear dielectric effects that originate from the absorption of energy from a high time-dependent electric field [20]. The liquid is assumed to consist of dynamically distinct domains within which the dielectric and the thermal relaxation proceed exponentially with a common time constant. If a sinusoidal external electric field,  $E(t) = E_0 \sin(\omega t)$ , is applied to a dielectric sample, a certain amount of energy  $Q$  will be transferred irreversibly to the sample of volume  $V$  per period, i.e. per time interval  $2\pi/\omega$  [21, 22]. The equivalent average power  $p_x$  absorbed from the external field is given by  $p_x = \varepsilon_0 E_0^2 \varepsilon''(\omega) V \omega / 2$ , where  $\varepsilon_0$  is the permittivity of vacuum and  $\varepsilon''(\omega)$  is the dielectric loss at the frequency of interest. The thermal relaxation time  $\tau_T$  specifies how the slow degrees of freedom relax their excess fictive temperature  $T_e$  ( $T_f = T_{\text{bath}} + T_e$ ). For steady

state conditions regarding the averages over one cycle, the heat balance yields

$$T_e = \frac{P_x}{\kappa} = \frac{\tau_T P_x}{C_p}. \quad (1)$$

Here,  $C_p$  is the relevant heat capacity and  $\tau_T$  is the thermal coupling time constant between the slow mode and the phonon bath. In the current approximation, the phonon temperature  $T_{\text{bath}}$  is assumed constant. Formally, the power representing the heat loss can be written in terms of the heat conductance  $\kappa$  between the slow mode and the phonon bath, with the relation to the thermal time constant given by  $\kappa = C_p/\tau_T$ . The effect of the fictive temperature on the relaxation time is quantified by the effective activation energy as derived from low-field  $\tau(T)$  data. The advantageous feature of this fictive temperature approach is the lack of adjustable parameters and the predictions reads

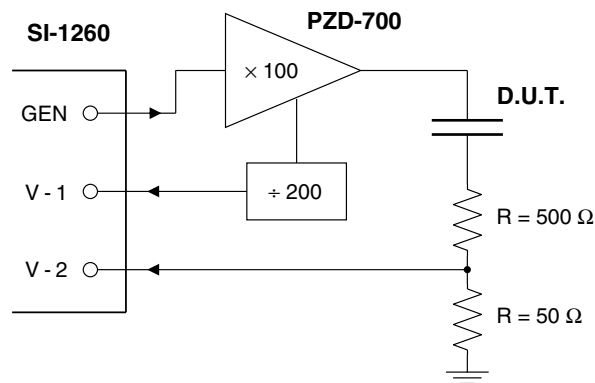
$$T_e(\tau) = \frac{\varepsilon_0 E_0^2 \Delta\varepsilon}{2\Delta c_p} \times \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} = T_e^0 \times \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}. \quad (2)$$

It is assumed here that a certain domain relaxes both the dielectric polarization and its excess heat with the same time constant, i.e.,  $\tau = \tau_D = \tau_T$  [23]. The leading term denoted  $T_e^0$  in (2) is  $\omega\tau$  independent, while the following term ranges between zero and unity, depending on the position of the relaxation time  $\tau$  relative to the frequency  $\omega$  of the applied harmonic field. For a given frequency  $\omega$ , this  $\omega\tau$  dependence implies that domains associated with slower relaxation,  $\tau \gg 1/\omega$ , will experience an increase of their fictive temperature by  $T_e^0$ , while faster modes with  $\tau \ll 1/\omega$  will remain unchanged. The value of  $T_e^0$  is readily determined by the electric field strength, dielectric relaxation amplitude, and heat capacity jump. In order to convert the  $T_e(\tau)$  effect to a change of the loss profile, the temperature effect is converted to a change in  $\ln \tau$  by virtue of the effective activation energy of the system. The complete loss spectrum at high fields is obtained by evaluating  $\tau^* = \tau + \Delta\tau$  via  $T_e(\tau)$  for each frequency  $\omega$  and then determining the distribution average according to

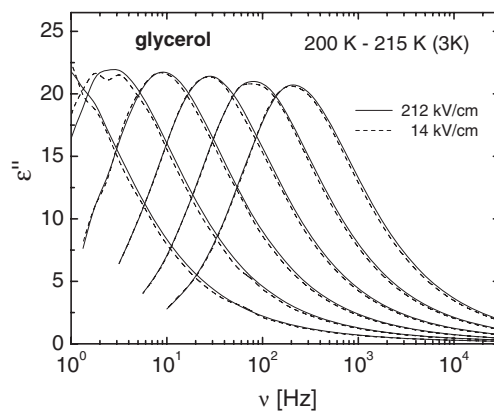
$$\varepsilon''(\omega) = \Delta\varepsilon \int_0^\infty g(\tau) \frac{\omega\tau^*}{1 + (\omega\tau^*)^2} d\tau. \quad (3)$$

### 3. Experiment

The liquids to be studied were purchased from Aldrich with the highest available purity and used as received. In order to determine the impedance at high electric ac fields, high voltages and thin samples are required. Samples are prepared between two lapped and polished brass electrodes (16 mm and 20 mm diameter), separated by a Teflon ring of 10  $\mu\text{m}$  thickness with 14 mm inner diameter and 20 mm outer diameter. The ring covers the edge of the smaller electrode completely, which appears to be advantageous for preventing field-related sample failures. The sample is held in a Novocontrol Quatro cryostat at the desired temperature. The impedance is determined by a Solartron SI-1260 gain/phase analyser, with the generator voltage amplified by a factor of 100 using a Trek PZD-700 amplifier. The voltage at the sample is recorded via input V-1 from the monitor output of the amplifier, the current is recorded via input V-2 as the voltage drop across a 50  $\Omega$  resistor. A 500  $\Omega$  resistor is used in series with the sample capacitor to protect the system against the voltages resulting from a dielectric breakdown. The 500  $\Omega$  resistor is calibrated and its value is subtracted from the measured impedance. The high-voltage part of the setup is outlined in figure 1. At each frequency, the high voltage is typically applied for 5 cycles, followed by a 20 cycle zero-field cooling period and by the lower-voltage measurement using  $E_0 = 14 \text{ kV cm}^{-1}$ , i.e. 10  $\text{V}_{\text{rms}}$  across 10  $\mu\text{m}$ . It has been checked that in all cases the number of high-field cycles used is sufficient to ensure the absence of significant



**Figure 1.** Experimental setup for impedance measurements at voltages up to 300 V based upon the Solartron SI-1260 gain/phase analyser. High voltages are provided by a Trek PZD-700 amplifier with built-in monitor signal for a direct return into the V-1 input. The current is measured at the V-2 input as voltage drop across a 50  $\Omega$  resistor. The 500  $\Omega$  resistor protects the input in the case of a shorted sample.

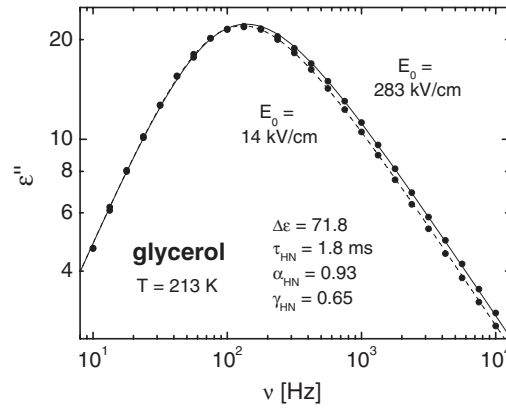


**Figure 2.** Experimental results for the dielectric loss  $\epsilon''(\nu)$  of glycerol for temperatures  $T = 200$ – $215$  K in steps of 3 K, in the order from low to high peak frequency. The pairs of curves are for two different fields,  $E_0 = 14$  kV cm $^{-1}$  (lower dashed curves) and at  $E_0 = 212$  kV cm $^{-1}$  (upper solid curves). The effect of an elevated electric field is to increase the loss of the high-frequency wing, while the spectrum below the peak frequency remains unchanged.

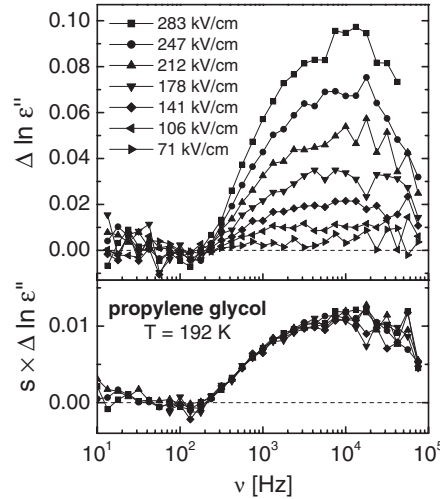
transient effects. Much longer application of the high field are avoided because this would increase the phonon temperature, which is assumed constant in the model.

#### 4. Results

A typical set of low- and high-field curves is shown in figure 2, where the dielectric loss of glycerol at various temperatures is measured for a low field of  $E_0 = 14$  kV cm $^{-1}$  and a much higher electric field of  $E_0 = 212$  kV cm $^{-1}$ . For the increased field, it is observed that the loss profile is subject to a substantial increase across the entire high-frequency wing, while the loss for lower frequencies remains field invariant. In figure 3, the same effect is displayed using a logarithmic  $\epsilon''$  scale for one temperature and a higher field of  $E_0 = 283$  kV cm $^{-1}$ , equivalent to 200 V $_{\text{rms}}$  across 10  $\mu\text{m}$ . The line for the  $E_0 = 14$  kV cm $^{-1}$  case is a Havriliak–Negami [24]



**Figure 3.** Experimental results (symbols) for the dielectric loss  $\epsilon''(\nu)$  of glycerol at  $T = 213$  K at fields of  $E_0 = 14 \text{ kV cm}^{-1}$  (lower data) and at  $E_0 = 283 \text{ kV cm}^{-1}$  (upper data). The line for the lower field is an HN fit with the parameters as indicated. The line for the higher field is the prediction of (2), without adjustable parameters. The relative signal increase at high frequencies is about 8.6%, while the measurement error does not exceed 0.2%.



**Figure 4.** Experimental results for the field-induced relative change of the dielectric loss,  $\Delta \ln \epsilon''(\nu)$ , for propylene glycol at  $T = 192$  K. The curves are for fields between  $E_0 = 71$  and  $283 \text{ kV cm}^{-1}$  in the order from bottom to top curve of the upper panel, as indicated. The lower panel shows the same data after rescaling by a factor  $s = E_{\text{ref}}^2 / E^2$ , i.e. with amplitudes scaled to a common field of  $E_{\text{ref}} = 100 \text{ kV cm}^{-1}$ .

(HN) fit with  $\alpha_{\text{HN}} = 0.93$ ,  $\gamma_{\text{HN}} = 0.65$ ,  $\tau_{\text{HN}} = 1.8 \text{ ms}$ , and  $\Delta\epsilon = 71.8$ . In this figure, it is more obvious that the field effect is a uniform relative increase, i.e.  $\Delta\epsilon''/\epsilon'' = \Delta \ln \epsilon''$  is approximately frequency invariant for  $\nu$  in excess of the peak frequency  $\nu_p$ . Similar results for propylene glycol (PG) are compiled with and without field normalization in figure 4, where the field range exceeds the glycerol case. From these PG results, the expected quadratic field dependence of the effect has been verified by averaging  $\Delta \ln \epsilon''(\nu)$  in the range from 422 Hz to 42.2 kHz for the different electric fields.

## 5. Discussion

In the case of large electric fields applied to single component liquids, the expected deviations from linear response behaviour are commonly based upon the Langevin effect, which reflects that dipole orientation and thus polarization will tend to saturate at sufficiently high fields. Based upon the dipole moment of glycerol,  $\mu = 2.56$  D, our highest fields of  $3 \times 10^7$  V m<sup>-1</sup>, and temperatures near  $T = 200$  K, the upper values of  $\mu E/kT$  are around 0.08. In the case of non-interacting dipoles, the Langevin function and its deviation from linearity,  $\langle \cos \theta \rangle = \mu E/3kT$ , yield a decrease of the susceptibility by 0.04%, while more detailed calculations could result in higher values. In any case, the present findings regarding the loss increase are incompatible with the effect of dielectric saturation, which should decrease the signal for all frequencies in the same fashion. At large time-dependent electric fields, some energy is transferred irreversibly from the electric field to the sample, but this is commonly not considered a significant source of nonlinear dielectric behaviour. However, additional energy will eventually increase the effective temperature of the system, which in turn leads to faster dynamics. A small temperature increase of the sample may be expected to result in a shift of the entire loss curve towards higher frequencies, again in contrast to our findings. However, the assumption of heterogeneous dynamics regarding dielectric as well as thermal relaxation changes the magnitude and frequency dependence of the ‘heating’ effects as quantified in the model outlined above.

The capability of the current model in terms of the loss measured at high fields is depicted in figure 3, where the upper solid line for the 283 kV cm<sup>-1</sup> case is derived from (2) and (3) without adjustable parameters. It is certainly instructive to elucidate further the origin of the field effects and its characteristic frequency dependence seen in figures 2–4. At a given frequency  $\omega_0 = 2\pi\nu_0$ , heat is provided to modes whose reciprocal relaxation time  $\omega = 1/\tau$  is not too remote from  $\omega_0$ . The amplitude of the power falls off symmetrically about  $\omega_0$ , but modes with  $\omega > \omega_0$  surrender their heat quickly to the phonons, while those with  $\omega < \omega_0$  accumulate much more heat before losing it to the bath. As a result, the loss of modes with  $\omega < \omega_0$  is shifted towards  $\omega_0$  and adds to the magnitude of  $\varepsilon''$  at the measurement frequency  $\omega_0$ . This rationale holds for all frequencies, except where no modes with  $\omega < \omega_0$  are available. That situation is found near the peak, where the probability density function  $g(\tau)$  for finding modes at a time constant  $\tau$  falls off dramatically towards large  $\tau$ . As an example, the dielectric Cole–Davidson distribution has no modes slower than the time constant parameter  $\tau_{CD}$ . This explains the absence of any such ‘heating’ effects for frequencies much below the position of the loss peak, including of course the steady state permittivity.

Compared with glycerol [20], very similar  $\Delta \ln \varepsilon''$  profiles are observed for the glass former PG in figure 4. The lower panel of that graph shows that the dependence of  $\Delta \ln \varepsilon''$  on the frequency is practically identical for all fields used. This is done by normalizing the curves to a reference field of  $E_{ref} = 100$  kV cm<sup>-1</sup> on the basis of the quadratic field dependence and observing a master curve. Therefore, the shape of  $\Delta \ln \varepsilon''(\nu)$  is field invariant, and shows some systematic deviations from the model behaviour which are yet to be explained. On the other hand, calculating the nonlinear effects as above but without the local coincidence of dielectric and thermal relaxation times (i.e. both quantities independently distributed) generates predictions which deviate strongly from the observed curves. The reason for this difference is the resulting combination of a small  $\tau_D$  with a large  $\tau_T$ , which leads to unrealistically high fictive temperatures in a fraction of the domains.

The most frequently considered source of nonlinear dielectric behaviour is polarization saturation or the Langevin effect. In the present cases, however, the absorption of energy is the only source of nonlinearity that had to be considered in order to rationalize the observations

regarding viscous glycerol and propylene glycol at sinusoidal electric fields up to  $300 \text{ kV cm}^{-1}$ . As a result, these experiments provide valuable information regarding the transfer of energy from the external electric field to the slow degrees of freedom and eventually to the phonon bath.

## 6. Conclusion

We have identified the absorption of energy from an external field by the slow modes as a significant source of nonlinear dielectric responses with unusually large deviations from linear behaviour. For two glass-formers, glycerol and propylene glycol, increases of the dielectric loss of up to 9% are observed for electric fields as high as  $283 \text{ kV cm}^{-1}$ . The effect is limited to frequencies in excess of the loss peak position, while the low-frequency permittivity and loss is not sensitive to this ‘heating’ effect. The key ingredient to rationalizing the findings is the heterogeneous nature of both dielectric and thermal relaxation times together with their local correlation.

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