

Nonlinear Dielectric Response and Thermodynamic Heterogeneity in Liquids

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If large amplitude time-dependent fields (e.g., dielectric, magnetic, mechanical) are applied to a sample that displays relaxational modes, some energy of the external field is absorbed by the slow degrees of freedom. The weak coupling of these modes to the phonon bath leads to long persistence times of the resulting higher fictive temperature. Assuming heterogeneities regarding dielectric and thermal relaxation times, extremely strong nonlinear dielectric effects are predicted and experimentally verified. For glycerol at $T = 213$ K, the dielectric loss measured at 280 kV/cm increases by more than 6% over its low-field value. This nonlinearity shows a characteristic frequency dependence and implies that dielectric and thermal time constants are locally correlated in viscous liquids.

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The disordered structure found in liquids, supercooled liquids, and glasses results in dispersive relaxation dynamics, usually observed as nonexponential correlation functions with which equilibrium is restored [1,2]. The recognition of heterogeneous dynamics in such systems has led to the picture of dynamically distinct domains with sizes of several nanometers, implying that the relaxation time is a spatially varying quantity. Dynamic heterogeneity has been probed mainly regarding the reorientational motion of molecules or polymer segments [3], using the techniques of nuclear magnetic resonance [4], deep photobleaching [5], dielectric hole burning [6–8], solvation dynamics [9], and computer experiments [10]. The majority of these experiments is performed in the viscous state near the glass transition temperature T_g [11], where relaxation time dispersions are most pronounced [12]. Less information is available regarding the heterogeneity of other more thermodynamic quantities such as dynamic heat capacity and enthalpy relaxation, although their relaxation times are also subject to considerable distributions [13]. While it is well established that both structural and thermodynamic variables display dispersive relaxation patterns, it is interesting to explore the extent to which their relaxation times are locally correlated.

Much of our knowledge of the behavior of glass-forming liquids is derived from relaxation experiments such as dielectric spectroscopy or dynamical mechanical analysis. In most cases, the applied external fields are safely within the regime of linear responses, so that the fluctuation-dissipation theorem applies and the observed correlation functions are directly related to the equilibrium fluctuations of the system [14]. Nonlinear dielectric effects have been studied as well, but mainly dielectric saturation (Langevin effect) or field induced chemical changes are considered as the sources of higher-order susceptibilities in simple liquids [15]. Dielectric hole burning (DHB) is a nonlinear method for studying spectral selectivity that exploits the effects of energy absorbed from the large external time-dependent electric field. To our knowledge, DHB is the only case where absorption of energy by the

slow degrees of freedom is employed to rationalize the nonlinear dielectric effects.

In this Letter, we present a prediction for nonlinear dielectric effects based solely on the slow degrees of freedom absorbing energy from the high-amplitude external field in a plain frequency-domain impedance measurement. Via the frequency dependent heat capacity, the absorbed energy is translated into an increased fictive temperature T_f , which in turn decreases the relaxation time τ according to the apparent activation energy, $\partial \ln \tau / \partial (1/T)$. For viscous glycerol, a significant increase of the dielectric loss of around 6% is calculated for a field of 280 kV/cm. The frequency dependence of this effect depends on whether dielectric and thermal relaxation times are assumed to be locally correlated. The predicted nonlinear dielectric effects are reproduced experimentally for glycerol at $T = 213$ K using peak electric fields between 140 and 280 kV/cm. We will use the term “nonlinear” not only with respect to the steady state quantities but also for any field dependence of the susceptibility $\hat{\chi}(\omega)$. The findings suggest that structural and thermodynamic relaxation times are both heterogeneous *and* locally correlated quantities, as assumed for rationalizing DHB results [6–8, 16–18]. While the individual dispersions are well documented, much less experimental support is available regarding their spatial correlation. It is often anticipated that all heat transport is governed by the value of the heat conductivity κ , which is in contrast to dispersive thermal relaxation times and persistent excess fictive temperatures. The present results show that the slow degrees of freedom are associated with heterogeneous κ 's with values much below the phonon counterpart.

For our model calculation, we follow the typical picture of heterogeneous dynamics and view the liquid as consisting of dynamically distinct domains within which the dielectric and the thermal relaxation proceeds exponentially with a certain time constant. The independence of the modes assumes that interactions among the dynamically distinct domains, e.g., exchange processes, remain small. For this situation, the frequency-domain dielectric relaxa-

tion function, $\hat{\varepsilon}(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega)$, can be expressed as a superposition of Debye processes,

$$\hat{\varepsilon}(\omega) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) \int_0^\infty g(\tau) \frac{1}{1 + i\omega\tau} d\tau, \quad (1)$$

where the probability density $g(\tau)$ reflects the relative number of relaxing units associated with dielectric time constants between τ and $\tau + d\tau$. For glycerol, it has been shown that $g(\tau)$ is virtually identical for dielectric relaxation $\hat{\varepsilon}(\omega)$ and for the dynamic heat capacity $\hat{c}_p(\omega)$ [19].

Consider a sinusoidal external electric field with frequency ω and amplitude E_0 applied to a dielectric sample, $E_x(t) = E_0 \sin(\omega t)$. Such a field will irreversibly transfer the amount of $Q = \pi\varepsilon_0 E_0^2 \varepsilon''(\omega) V$ of energy to the sample of volume V per period, i.e., per time interval $2\pi/\omega$ [20,21]. The equivalent average power p_x absorbed from the external field is given by

$$p_x = \frac{Q\omega}{2\pi} = \frac{\varepsilon_0 E_0^2 \varepsilon''(\omega) V \omega}{2}, \quad (2)$$

where ε_0 is the permittivity of vacuum, and $\varepsilon''(\omega)$ is the dielectric loss at the frequency of interest. In the majority of experimental situations, the effect of this heat transfer is considered negligible. At sufficiently high fields, however, the absorbed energy should be expected to modify the susceptibility and thereby give rise to nonlinear effects. Because the slow degrees of freedom which absorb the energy are not strongly coupled to the phonon bath [22], the resulting excess fictive temperature $T_e(T_f = T_{\text{bath}} + T_e)$ will relax at the thermal relaxation time τ_T . In the case of steady state conditions regarding the averages over one cycle, the heat balance equation reads

$$C_p \frac{dT_e}{dt} = 0 = p_x - \kappa T_e = p_x - \frac{C_p T_e}{\tau_T} \Rightarrow T_e = \frac{p_x}{\kappa} = \frac{\tau_T p_x}{C_p}. \quad (3)$$

Here, C_p is the relevant heat capacity and τ_T is the thermal coupling time constant between the slow mode and the phonon bath. Formally, the power representing the heat loss can be written in terms of the heat conductance κ between the slow mode and the phonon bath, with the relation to the thermal time constant given by $\kappa = C_p/\tau_T$. Here, the time dependence is cast into the heat flow and the heat capacities are used without explicit time dependence. For simplicity, the phonon temperature T_{bath} is assumed constant. Finally, how the temperature alters the relaxation time is quantified by the effective activation energy $E_A^{\text{eff}} = d(\ln\tau)/d(1/k_B T)$ as derived from low-field $\tau(T)$ data. The advantageous feature of this fictive temperature approach is the lack of adjustable parameters, but it could be translated into the concept of field dependent barrier heights.

For the dynamically distinct domains associated with a certain time constant τ , both the heat capacity and the

dielectric loss are assumed proportional to the number of molecules, $g(\tau)d\tau$. The loss component for a particular dielectric relaxation time τ_D is a Debye profile given by

$$\varepsilon''(\omega) = \Delta\varepsilon \frac{\omega\tau_D}{1 + \omega^2\tau_D^2} g(\tau_D) d\tau_D, \quad (4)$$

where $\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$ is the dielectric relaxation strength, i.e., the difference between the dielectric constants in the limits of low (ε_s) and high (ε_∞) frequency. Similarly, the volumetric heat capacity of the domains characterized by a certain thermal relaxation time τ_T is given by

$$c_p = C_p/V = \Delta c_p g(\tau_T) d\tau_T, \quad (5)$$

where Δc_p is the total heat capacity step associated with the slow modes, $\Delta c_p = c_{p,s} - c_{p,\infty}$, with $c_{p,s}$ being the steady state value and $c_{p,\infty}$ the heat capacity of the phonon bath [23]. Combining Eq. (2) through Eq. (5) yields for the excess temperature

$$T_e(\tau) = \frac{\varepsilon_0 E_0^2 \Delta\varepsilon}{2\Delta c_p} \frac{\omega^2 \tau_D \tau_T}{1 + \omega^2 \tau_D^2}. \quad (6)$$

As justified previously [24], we will assume additionally that a certain domain relaxes both the dielectric polarization and its excess heat with the same time constant, i.e., $\tau = \tau_D = \tau_T$. This simplifies Eq. (6) to

$$T_e(\tau) = \frac{\varepsilon_0 E_0^2 \Delta\varepsilon}{2\Delta c_p} \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} = T_e^0 \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2}. \quad (7)$$

The first term after each equal sign is an $\omega\tau$ independent constant denoted T_e^0 , while the second terms range between zero and unity, depending on the position of the relaxation time τ relative to the frequency ω of the applied harmonic field $E_x(t)$. This $\omega\tau$ dependence is shown in Fig. 1. For a given frequency ω , the curve 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.

To estimate the magnitude of the effect in glycerol, we use the dielectric relaxation strength of $\Delta\varepsilon = 72$, the heat capacity contribution $\Delta c_p = 1.5 \text{ J K}^{-1} \text{ cm}^{-3}$ [13], and a field of $E_0 = 280 \text{ kV/cm}$, which results in an excess temperature limit of $T_e^0 = 0.18 \text{ K}$. Based on the activation energy of $E_A/k_B = 20000 \text{ K}$, this value of T_e^0 translates into a relative relaxation time change of $\Delta\tau/\tau = \Delta \ln\tau = -0.10$. For the high frequency wing of the loss of glycerol, the slope is $d \ln\varepsilon''/d \ln\omega \approx -0.55$, which will result in an increase of the loss reaching $\approx 6\%$. The complete loss spectrum at high fields is obtained by evaluating $\tau^* = \tau + \Delta\tau$ via $T_e(\tau)$ for each frequency ω and then determining the average over $1/(1 + i\omega\tau^*)$ as in Eq. (1).

In order to observe the above effect, a sample of glycerol (Aldrich, 99.5 + %) is prepared between two brass electrodes (16 and 20 mm diameter), separated by a Teflon ring of 10 μm thickness. The sample is held in a Novocontrol Quatro cryostat at a temperature of $T = 213 \text{ K}$. The im-

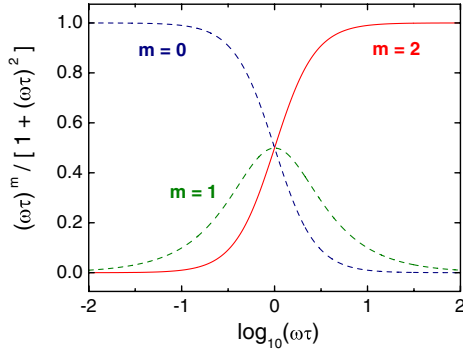


FIG. 1 (color online). Dependence of the relative “heating” effect on relaxation time constant τ relative to the frequency $\omega = 2\pi\nu$ of the electric field, $(\omega\tau)^m/[1 + (\omega\tau)^2]$ for $m = 2$ (solid line) versus $\omega\tau$. For a comparison, the dashed lines represent the storage ($m = 0$) and loss ($m = 1$) components of a Debye-type process.

pedance is determined by a Solartron SI-1260 gain/phase analyzer, with the generator voltage amplified by a factor of 100 using a Trek PZD-700. The voltage at the sample is recorded via input V1 from the monitor output of the amplifier; the current is recorded via input V2 as the voltage drop across a 50Ω resistor. A 500Ω resistor is used in series with the sample capacitor to protect the system against a dielectric breakdown, and its value is subtracted from the measured impedance. At each frequency, the high voltage is typically applied for 5 cycles, followed by a 20 cycle cooling period and by the lower voltage measurement using $E_0 = 14$ kV/cm. The lower

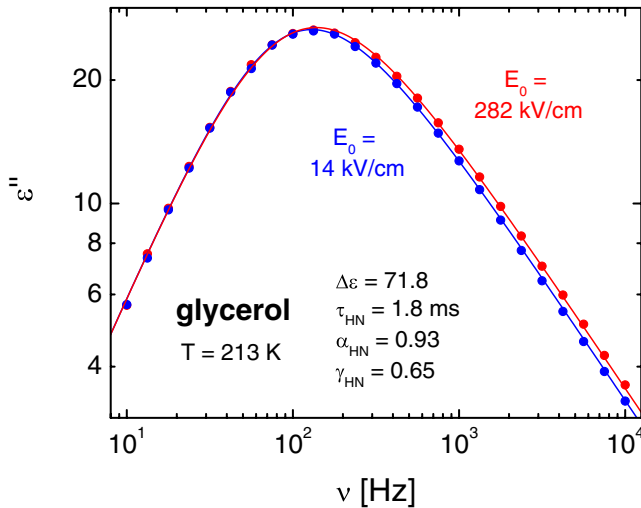


FIG. 2 (color online). Experimental results (symbols) for the dielectric loss $\epsilon''(\nu)$ of glycerol at $T = 213$ K at fields of $E_0 = 14$ kV/cm (lower data) and at $E_0 = 282$ kV/cm (higher data). The line for the lower field is a HN fit with the parameters as indicated. The line for the higher field is the prediction of Eq. (7), without adjustable parameters. The relative signal increase at high frequencies is about 8.6%, while the measurement error does not exceed 0.2%.

trace of symbols in Fig. 2 represents the loss obtained at the low field of $E_0 = 14$ kV/cm. The line is a Havriliak-Negami [25] (HN) fit with $\alpha_{\text{HN}} = 0.93$, $\gamma_{\text{HN}} = 0.65$, $\tau_{\text{HN}} = 1.8$ ms, and $\Delta\epsilon = 71.8$. The upper symbols reflect the results for a high field of $E_0 = 282$ kV/cm, equivalent to $200 V_{\text{rms}}$ across $10 \mu\text{m}$. The line is the loss derived from the present model, assuming $\tau_T = \tau_D$ as in Eq. (7), i.e., for correlated structural and thermodynamic relaxation times. Note that this excellent agreement is achieved without an adjustable parameter.

The loss profile is not field dependent for frequencies below the peak position ω_{max} , because at $\omega < \omega_{\text{max}}$ there are simply no time constants with $\tau > 1/\omega$ that could accumulate the energy. (Note that the HN distribution decreases sharply for $\tau > \tau_{\text{HN}}$.) Accordingly, the steady state dielectric constant ϵ_s will not be affected by this field “heating.” For the higher frequencies, the magnitude of this nonlinear effect is unusually large, due to the fact that the slower modes with $\tau \gg 1/\omega$ can accumulate the energy absorbed over many cycles before it is released to the phonon bath. Incidentally, relative changes $\Delta\epsilon''/\epsilon''$ of up to 30% and a shift of the peak loss position were observed in the case of continuous application of the high field, presumably due to a net increase of the phonon temperature. Therefore, short high-field intervals with sufficient cooling time is required to obtain consistency with the model which uses a constant phonon temperature.

For three field amplitudes the observed nonlinear features are shown in more detail as $\Delta \ln \epsilon''$ versus frequency ν in Fig. 3. The solid lines are the model predictions assuming $\tau_T = \tau_D$ as in Eq. (7). The dashed lines are based upon Eq. (6) with a constant average thermal relaxation $\tau_T = \tau_{\text{av}}$ ($\tau_{\text{av}} \approx \tau_{\text{HN}} \gamma_{\text{HN}}$ [26]) and demonstrate the effect of

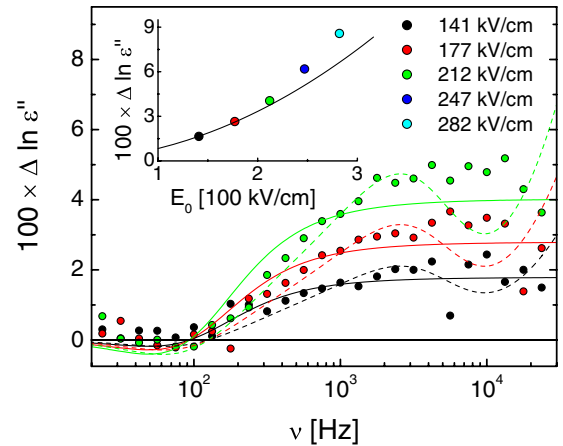


FIG. 3 (color online). Experimental results (symbols) for the field induced relative change of the dielectric loss, $\Delta \ln \epsilon''(\nu)$, for fields of $E_0 = 141$, 177 , and 212 kV/cm in the order from bottom to top curve. The solid and dashed lines represent the predictions of Eq. (7) ($\tau_T = \tau_D$) and Eq. (6) with $\tau_T = \tau_{\text{av}}$, respectively. The inset shows the field dependence of the $\Delta \ln \epsilon''$ plateau value: symbols are obtained by averaging the data in the $\nu \geq 10^3$ Hz range; the line is derived from Eq. (7).

removing the local identity of thermal and dielectric relaxation times. The resulting combination of fast dielectric and slow thermal properties leads to unrealistic heat accumulation which is responsible for the different frequency dependence. The present data are more consistent with the assumption of thermal and dielectric relaxation being heterogeneous and locally correlated, because no indication is found for the dip at 10^4 Hz and the sharp rise at higher frequencies. As shown in the inset of Fig. 3, the present nonlinearity, $\Delta \ln \epsilon''$, follows a quadratic field dependence as expected, with increasing deviations above 200 kV/cm again suggesting additional phonon bath heating. While an improved signal-to-noise ratio regarding $\Delta \ln \epsilon''(\nu)$ is desirable, high voltage impedance measurements are clearly capable of providing valuable information regarding the heterogeneity of the modes that contribute to heat capacity, the quantity that is most commonly used to identify the glass transition. While dynamic heat capacity measurements probe the heat flow from the phonon bath into the slow modes, this dielectric heating experiment requires the understanding of how the slow degrees of freedom surrender their excess energy to the phonons. In this respect, the present features are similar to DHB experiments [7] and model calculations of large amplitude dielectric step-response experiments [24], and complimentary to dynamic heat capacity experiments.

Nonlinear dielectric effects are more typically studied using liquid crystals [27] or binary systems [28]. In the case of simple liquids, the expected nonlinearities such as Langevin or chemical effects remain small and the heating induced changes observed here have not been considered as a significant contribution. The use of large static bias fields will avoid this heating, but experiments involving time-dependent electric fields of high amplitude are likely to display polarizations which are modified by the absorption of energy. As an example, time resolved studies of nonlinear dielectric effects have been performed with strong time-dependent electric fields by Rzoska *et al.* on epoxy samples [29,30].

In the present case of viscous glycerol at harmonic electric fields not exceeding 300 kV/cm, the heating induced change of the response is the only nonlinearity that had to be considered in order to rationalize the observations. Most interestingly, the details of the higher-order susceptibilities depend on how the excess energy is transferred from the slow degrees of freedom to the phonon bath and whether these thermal relaxation times are locally correlated with the time constants of structural relaxation. Similarly, the heating effects discussed here will also occur in other experimental approaches such as magnetic or mechanical measurements if performed beyond the linear response regime. A further interesting variant of this high-field impedance approach to thermodynamic heterogeneity would be to probe the susceptibility at frequencies which differ from that of the large amplitude signal.

In conclusion, we have identified the absorption of energy from an external field by the slow modes as a significant source of nonlinear responses with unusually large higher-order susceptibilities. Additionally, a “simple” impedance experiment is shown to provide novel insight into thermodynamic heterogeneity and nanoscale energy transfer in amorphous materials.

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