

## On the low frequency loss peak in the dielectric spectrum of glycerol

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We measured dielectric spectra of glycerol at pressures exceeding 1 GPa in order to examine the slow Debye-like peak. This peak is not a relaxation process, but its frequency is consistent with an origin in dielectric discontinuities due to impurities. These heterogeneities have a non-negligible bulk modulus and are identified as volatile, relatively non-polar liquid contaminants. Although this slow peak is often found in the dielectric spectra of polyalcohols, it is not an intrinsic feature thereof, unlike the ostensibly similar relaxation peak in monoalcohols. [doi:10.1063/1.3629449]

Recently there has been a flurry of activity directed at identifying the origin of a peak in the dielectric loss of polyalcohols that falls at frequencies lower than the structural  $\alpha$ -relaxation.<sup>1-9</sup> The salient facts concerning this low frequency peak are

- (i) It has a qualitative correspondence to the well-established Debye peak in monohydroxy alcohols, which is also lower in frequency than the  $\alpha$ -relaxation but had been regarded as unique to monoalcohols.<sup>10-13</sup>
- (ii) Unlike for monoalcohols, the loss peak in polyalcohols is weaker than the  $\alpha$ -peak and cannot be directly observed due to masking by dc-conductivity,  $\sigma$ .<sup>1-4</sup>
- (iii) Extended exposure of a polyalcohol sample to vacuum diminishes the peak intensity.<sup>9</sup>
- (iv) The frequency of the peak roughly corresponds to the frequency at which the real,  $\epsilon'$ , and imaginary,  $\epsilon''$ , components of the dielectric permittivity are equal. It follows that addition of ions, which increases  $\sigma$ , shifts the peak to higher frequencies.<sup>9</sup>
- (v) In some spectra of polyalcohols, the peak is absent.<sup>8</sup>

This polyalcohol peak has been ascribed to relaxation of “clusters”;<sup>1-3,5,7</sup> however, based primarily on the facts listed above, Richert *et al.*<sup>9</sup> concluded that the peak is not a relaxation process, and, indeed, has no intrinsic connection to the dynamics. Rather, it was suggested that the presence of heterogeneities in the liquid, specifically gaseous bubbles,<sup>9</sup> gives rise to dielectric discontinuities, which contribute a capacitance and consequent peak at a frequency associated with ion mobility (i.e., in the vicinity of the conductivity relaxation frequency, at which  $\epsilon' \approx \epsilon''$  (Ref. 14)). However, because the peak is weak and falls at low frequencies, its observation requires removal of the dc-conductivity, either by subtraction from the loss spectrum or by analyzing the derivative of  $\epsilon'$ . In the sense that this peak arises from the sample, it is not an artifact, unlike spurious features in dielectric spectra due to electrode polarization, cable effects, etc.

In this article we report dielectric spectra of glycerol (from Fluka, with water content <0.8 wt.%), measured at pressures up to 1.12 GPa. The data are in accord with the conclusion of Ref. 9 that the slow peak is not a dipole relaxation process, but is due to dielectric discontinuities within the material. However, our results indicate that these heterogeneities have a liquid-like bulk modulus ( $\sim$ GPa); thus, they cannot be air bubbles (bulk modulus  $\sim$ 0.1 MPa). Consistent with all available experimental findings, the heterogeneities are identified as volatile, liquid contaminants. Their immiscibility with glycerol suggests relatively non-polar character, whereby their dynamics *per se* are not evident in the dielectric spectra.

Figure 1 (top panel) shows  $\epsilon'$  and  $\epsilon''$  for glycerol at  $T = 295.6$  K. With increasing pressure there is a systematic shift of the conductivity, and the appearance at higher frequencies of the low frequency wing of the  $\alpha$ -relaxation peak. In the lower panel of Fig. 1 is the derivative function,  $-(\pi/2) \times (d\epsilon'/d \ln \omega)$ , which is an approximation to the dielectric loss absent the conductivity contribution (but not the electrode polarization).<sup>15</sup> The derivative function spectrum shows a distinct peak at ambient pressure around  $f = 800$  Hz. As pressure increases, the peak shifts to lower frequency and increases in amplitude. Fitting the peak to the derivative of the Havriliak-Negami function,<sup>16</sup> we obtain the dielectric strength, which is plotted in the inset versus pressure. (Note that since the derivative of  $\epsilon'$  deviates more from the actual loss peak as the latter becomes narrower, for a Debye-like peak it is necessary to use the derivative of the relaxation function to fit the  $-d\epsilon'/d \ln \omega$  peak.) The dielectric strength *increases* with pressure, with a substantial intensity even at 1.12 GPa, indicating a significant bulk modulus for the heterogeneities. This is inconsistent with their identification as bubbles, which of course would show the opposite behavior. Note that small bubbles could give rise to a pressure difference with the surrounding fluid (Young-Laplace effect), potentially stabilizing them to pressure. However, non-polar liquids have typical surface tensions on the order of 24 N/mm, so that even a 0.1  $\mu$ m bubble would have a difference between internal and external pressures of only 0.5 MPa, three orders of magnitude smaller than the highest pressure in Fig. 1.

The peak frequency shifts in accord with the change of the conductivity relaxation frequency, denoted by the vertical dashed lines, the decrease in  $\sigma$  with pressure moving the

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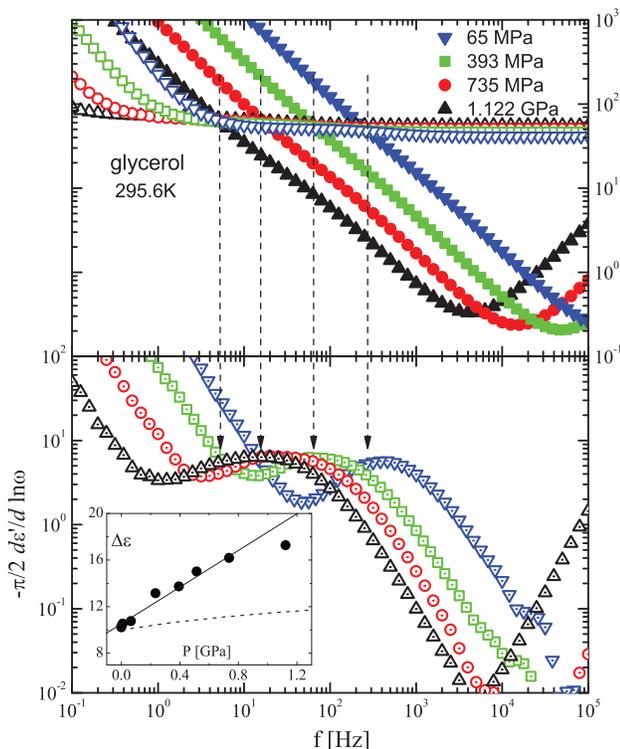


FIG. 1. (Top panel) Real (open symbols) and imaginary (filled symbols) permittivity, the low frequency rise in  $\epsilon'$  due to electrode polarization, and the high frequency rise in  $\epsilon''$  due to the  $\alpha$  process. The vertical arrows indicate frequency at which  $\epsilon' = \epsilon''$ . (Lower panel) Derivative function revealing the slow process masked in  $\epsilon''$  by the conductivity. Inset shows dielectric strength determined by fitting derivative of a Havriliak-Negami function to the data; error bars are no larger than the symbol size. The solid line is the linear fit to the data, and the dotted line is the change in  $\Delta\epsilon$  due to only density changes, assuming a constant Kirkwood correlation parameter.

intersection point  $\epsilon' = \epsilon''$  to lower frequency. The full width at half maximum (FWHM) of the peak at the lowest pressure is 1.17 decades, very close to that of a Debye process (FWHM = 1.14); with increasing pressure the FWHM increases to 1.45 decades.

According to the classical treatment of Sillars,<sup>17</sup> for a volume fraction of spheres  $v_2 \ll 1$ , having permittivity  $\epsilon_2$  and conductivity  $\sigma_2$  in a matrix of permittivity  $\epsilon_1$  and conductivity  $\sigma_1$ , there is a dispersion having the shape of a Debye peak with a dielectric strength  $\Delta\epsilon_D$  given by<sup>16</sup>

$$\Delta\epsilon_D = \frac{9(\epsilon_2\sigma_1 - \epsilon_1\sigma_2)^2 v_1 v_2}{[2\epsilon_1 + \epsilon_2 + (\epsilon_1 - \epsilon_2)v_2][2\sigma_1 + \sigma_2 + (\sigma_1 - \sigma_2)v_2]^2} \quad (1)$$

and relaxation time  $\tau_D$

$$\tau_D = \epsilon_0 \frac{2\epsilon_1 + \epsilon_2 + v_2(\epsilon_1 - \epsilon_2)}{2\sigma_1 + \sigma_2 + v_2(\sigma_1 - \sigma_2)}, \quad (2)$$

where  $\epsilon_0$  is the permittivity of vacuum. For  $\sigma_2 \ll \sigma_1$  and  $\epsilon_2 \ll \epsilon_1$ ,  $\tau_D = \epsilon_0\epsilon_1/\sigma_1$ , which corresponds to  $\tau_D = 2\pi f_{\epsilon'_1=\epsilon''_1}$ , and from Eq. (1) it follows that  $\Delta\epsilon_D$  is approximately proportional to  $\epsilon_1$ . This is in accord with the linearity of  $\Delta\epsilon_D$  for the Debye process (inset to Fig. 1). We observed a proportional increase of  $\sim 40\%$  with pressure in the static value of

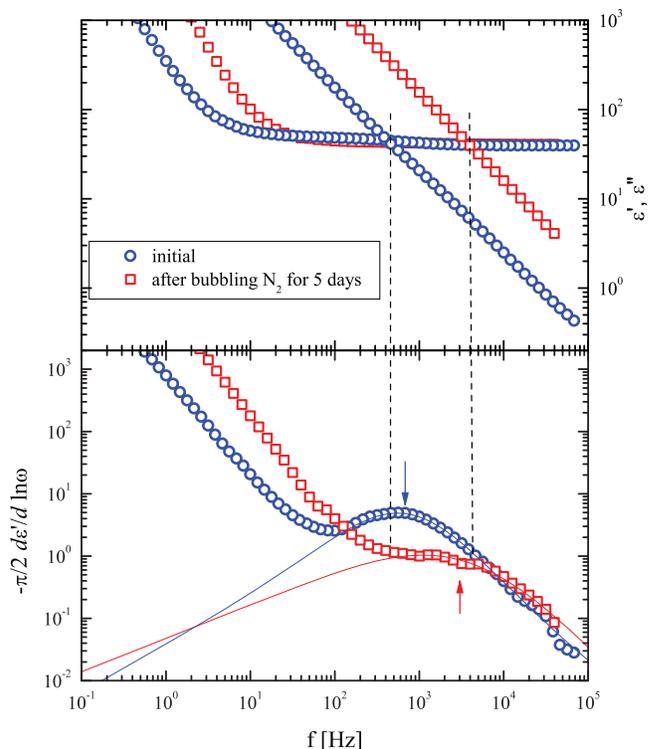


FIG. 2. Glycerol before and after bubbling nitrogen for 5 days at  $T = 295.6$  K. (Top panel) Real and imaginary parts of the permittivity. The vertical dotted lines indicate the frequency at which  $\epsilon' = \epsilon''$ . (Lower panel) Derivative function  $\epsilon'$ . Solid lines are best fit of the derivative of a Havriliak-Negami function. Arrows indicate  $(2\pi\tau_{HN})^{-1}$ , where  $\tau_{HN}$  is the Havriliak-Negami relaxation time.

the dielectric constant (determined at  $f = 20$  kHz, intermediate between the low frequency and  $\alpha$  dispersions). Thus, the behavior of the Debye peak at high pressure is consistent with that originating from dielectric discontinuities in the sample, these contaminants having a bulk modulus on the order of that of glycerol, i.e., much larger than that of a gas. Assuming the heterogeneities are relatively non-polar (accounting for their immiscibility with the glycerol), the low strength of the measured Debye process (Fig. 1) requires  $\sigma_2 > \sigma_1$ . This moves the peak frequency away from  $f_{\epsilon'_1=\epsilon''_1}$ , as observed in the figure. Note, however, that quantitative inferences from Eq. (1) are limited since specific information about the contaminant(s) properties and concentration are lacking. Moreover, this interpretation is not completely satisfactory since to obtain values close to the measured value of  $\Delta\epsilon_D$  for  $\sigma_2 \ll \sigma_1$ , and  $\epsilon_2 \ll \epsilon_1$ , Eq. (1) would require  $v_2$  to be larger than a few percent, which seems unlikely. The discrepancy is due to the assumption of Eq. (1) of a homogenous distribution of heterogeneities. Any accumulation of the impurities in the vicinity of the electrodes (potentially even forming a thin layer), would increase  $\Delta\epsilon_D$  substantially, while maintaining the condition  $\tau_D = 2\pi f_{\epsilon'_1=\epsilon''_1}$ .

Following Ref. 9, in which it was shown that the intensity of this peak diminished after exposure to vacuum, we applied two treatments to the glycerol: bubbling of nitrogen gas for 120 h (Fig. 2) and exposure to vacuum for 44 h. Both treatments caused a *reduction* in the amplitude and some

broadening of the peak, but not its disappearance. The dielectric strength decreases by 67% and 77%, respectively, and the FWHM increased to 1.92 and 1.32. The obvious interpretation is that the heterogeneities are composed of a liquid having some volatility (and thus removable either by bubbling of nitrogen through the sample or evacuation), but they cannot be gaseous since purging would cause the opposite behavior. Although crystalline impurities would also constitute a dielectric heterogeneity, they would be unaffected by purging with gas or evacuation and less affected by pressure than liquid contaminants. The increase in conductivity after either treatment is tentatively ascribed to an increase of ion diffusion into the bulk glycerol as the occlusions are removed.

Finally we note that the sample thickness for the measurements herein was 1.5 mm. Experiments were also carried out with an electrode separation of 0.1 mm; however, this gave greater electrode polarization, manifested as a more prominent rise in  $\epsilon'$ , interfering with observation of the low frequency peak.

In summary, the present results affirm the low frequency Debye peak in glycerol to be a consequence of heterogeneities, unrelated to any molecular dynamics. These dielectric discontinuities give rise to a weak peak at frequencies associated with the conductivity relaxation. Their non-negligible bulk modulus, decreasing amplitude when nitrogen is bubbled through the sample, and resistance to evaporation identify the species as weakly or non-polar, immiscible liquid contaminants. They cannot be primarily bubbles, since the application of high pressure enhances the strength of the Debye peak, rather than causing its disappearance. Thus, this low frequency peak, although widely occurring, is not a

general feature of the dielectric behavior of polyalcohols, nor can it be related to the Debye process in monoalcohols.

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