



ELSEVIER

Journal of Non-Crystalline Solids 172-174 (1994) 357-361

JOURNAL OF  
NON-CRYSTALLINE SOLIDS

# Comparative measurements of the electrical and shear mechanical response functions in some supercooled liquids

T. Christensen\*, N.B. Olsen

*IMFUFA, Roskilde University Center, Postbox 260, DK-4000 Roskilde, Denmark*

## Abstract

The frequency dependences of the shear modulus,  $G_s(\omega)$ , (10 Hz–60 kHz) and dielectric constant,  $\varepsilon(\omega)$ , (10 Hz–10 MHz) have been measured at various temperatures. Two different liquids have been studied: the polyalcohol 1, 3-Butandiol which has a large dielectric relaxation strength and a silicone oil with a very small relaxation strength. It is shown that the normalized relaxational part of the inverse dielectric susceptibility and the mechanical shear modulus are identical for both liquids, while the loss peak frequencies are different.

## 1. Introduction

Normally a given material property defines more than one relaxation function. For pure mathematical reasons, these functions often have different shapes. One should therefore take care when comparing loss peak frequencies, Kohlrausch parameters, etc. for different response functions, as for instance dielectric and mechanical responses.

In the following, we define the electrical susceptibility as  $\chi = \varepsilon - 1$ , and the electrical modulus,  $G_e$ , as the inverse of  $\chi$ . These two response functions define two relaxation functions of different shapes. Note that  $G_e$  is different from the electric modulus function,  $M$ , normally defined as the inverse of  $\varepsilon$  [1], and also that  $M(\omega)$  and  $G_e(\omega)$  have different shapes. The reason why we nevertheless here

choose  $G_e$  is that this response function is linear in the reciprocal microscopic polarizability both for strong (large  $\chi$ ) and weak (small  $\chi$ ) dipolar interactions as seen from Clausius–Mossotti relation. Dyre [2] has earlier discussed some of the problems of interpreting data in terms of  $M$ .

The aim of this work is to compare the mechanical and electrical properties for two types of liquid, one with a large and one with a small relaxation strength, and to find the response functions appropriate for a comparison.

Only a few attempts have been published comparing the shear mechanical and dielectrical relaxation functions. The theory Debye [3] is based on a model consisting of non-interacting permanent dipoles in a viscous liquid, the viscosity of which is independent of frequency. In this model, the microscopic dipolar polarizability is given by a simple relaxation function,  $\alpha(\omega)$ , with a relaxation time,  $\tau$ , where

$$\tau = 8\pi\eta R^3/k_B T, \quad (1)$$

\* Corresponding author: Tel: +45 4675 7711, ext. 2276, Telefax: +45 4675 5065. E-mail: tec@mmf.ruc.dk.

$R$  being the molecular radius and  $\eta$  the shear viscosity, and with  $\alpha(\omega)$  given by

$$\alpha(\omega) = \mu^2 / (3k_B T(1 - i\omega\tau)), \quad (2)$$

where  $\mu$  is the permanent dipole moment of the molecule. In the Clausius–Mossotti approximation,  $\chi$  is related to  $\alpha$  as

$$\chi(\omega) / (\chi(\omega) + 3) = \frac{4}{3} \pi n \alpha(\omega), \quad (3)$$

where  $n$  is the density of dipoles.

The fact that Eq. (1) often gives reasonable values for  $R$  shows that shear mechanical and dielectrical properties are related at least for liquids with permanent dipoles.

DiMarzio and Bishop [4] have proposed a general relationship between  $\varepsilon$  and the shear modulus,  $G_s$ , as follows:

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + KG_s(\omega)}$$

where

$$K = \frac{4\pi R^3(\varepsilon_0 + 2)}{k_B T(\varepsilon_\infty + 2)}. \quad (4)$$

This equation was derived from a generalization of the Debye model, together with the Clausius–Mossotti approximation relating  $\varepsilon$  to the dipolar polarizability. Eq. (4) directly gives a relation between the two response functions, which can be verified experimentally. This equation however cannot be exact in the limit  $\omega \rightarrow \infty$ , since  $G_s$  is a bounded function of  $\omega$ .

## 2. Experimental

The dielectric measurements were carried out using a HP4192A impedance analyzer. The measuring cell consists of a gold-coated multi-plate condenser with a capacitance  $C_0 = 68.0$  pF. The capacitance of the liquid-filled capacitor was measured in the frequency range 10 Hz–10 MHz.

In the shear mechanical measurements, a piezoelectric transducer cell was used, enabling one to measure the complex shear modulus in the frequency interval 10 Hz–60 kHz. In this new measuring technique [5], the shear modulus is calculated

directly from the measured capacitance of the empty and the liquid-filled transducer. The transducer consist of three piezoceramic discs with thickness  $t = 0.5$  mm and radius  $r = 10.0$  mm in a sandwich structure, and with a spacing  $d = 0.5$  mm. If the free spacing is filled with a liquid, the piezoceramic discs will be partly clamped, depending on the shear rigidity of the liquid. In this way, the capacitance of the transducer depends on the shear modulus of the liquid in a calculable way, and  $G_s$  can be determined with an uncertainty of 10% in a rigidity interval of 10 MPa–10 GPa. Using the HP impedance analyzer, the relative frequency dependence of  $G_s$  is determined with an uncertainty of 2% between 100 Hz and 10 kHz, with a strain amplitude below  $10^{-6}$ .

Much care has been exercised to control the liquid under examination. Thus the absolute temperature is controlled within 0.2 K in the two different measuring cells. The temperature stability of the cryostat, which is used in both types of measurement, is better than 5 mK. Two liquids have been studied: the polyalcohol 1, 3-Butandiol (Fluka AG. purum) and a silicone oil (MS704 used for diffusion pumps). Since 1, 3-Butandiol adheres water, the same bottle of liquid was used, and the measurements were performed in rapid succession. The silicone oil is very stable, and measurements on the mechanical and electrical properties are very reproducible.

## 3. Results

For both liquids, the electrical measurements show that the strength of the relaxational part of the susceptibility varies roughly proportional to the inverse temperature. For 1, 3-Butandiol, one has  $\chi(\infty) = 1.90$  and  $\chi(0) = 44.9$  and 206 K and for silicone oil  $\chi(\infty) = 1.65$  and  $\chi(0) = 1.85$  at 232 K. The two liquids thus have a large and a small relaxation strength, respectively. The infinite frequency shear modulus was relatively small for both liquids, namely for 1, 3-Butandiol  $G_s(\infty) = 1.80$  GPa at 190 K and for silicone oil  $G_s(\infty) = 0.98$  GPa at 227.5 K.

In order to compare different relaxation functions, an ‘Argand diagram’ is often preferable in

favour of a frequency plot, since a 'master curve' in this diagram is produced without a scaling of the frequency. Thus the temperature-timescale principle in this way can be directly justified.

The shapes of the three normalized electrical relaxation functions derived from  $\chi$ ,  $G_e$  and  $M$  are shown in Fig. 1, revealing a substantial difference between the susceptibility and the two modulus functions. The latter two differ only slightly but are discernable. The corresponding plot for the silicone oil is not shown since all three functions in this case have nearly the same shape. This is because the relaxation strength of this liquid is much smaller than  $\chi(\infty)$ .

Figs 2 and 3 show a comparison of the normalized shear modulus,  $G_{sn}$ , and the relaxational part of the electric modulus,  $G_{en}$ . It is seen that the difference between  $G_{sn}$  and  $G_{en}$  is much smaller than the difference between  $G_{en}$ ,  $M_n$  and  $\chi_n$  shown in Fig. 1. The observed slight deviation between  $G_{en}$  and  $G_{sn}$  is within the experimental error.

The loss peak frequency,  $f_p$ , was determined by fitting a second order polynomial to the datapoints around the absolute maximum point.

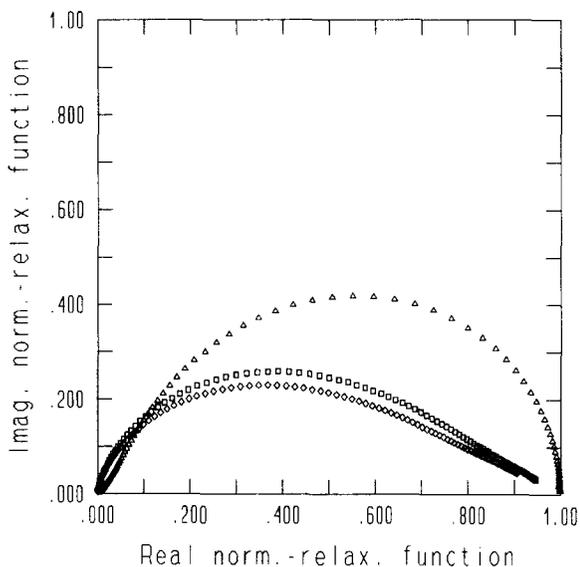


Fig. 1. Dielectric measurements on 1,3-Butandiol at 194 K. The three curves represents the normalized relaxational part of the following three response functions:  $\Delta$ , susceptibility  $\chi_n$ ;  $\diamond$ , the inverse of the susceptibility  $G_{en}$ ;  $\square$ , modulus  $M_n$ .

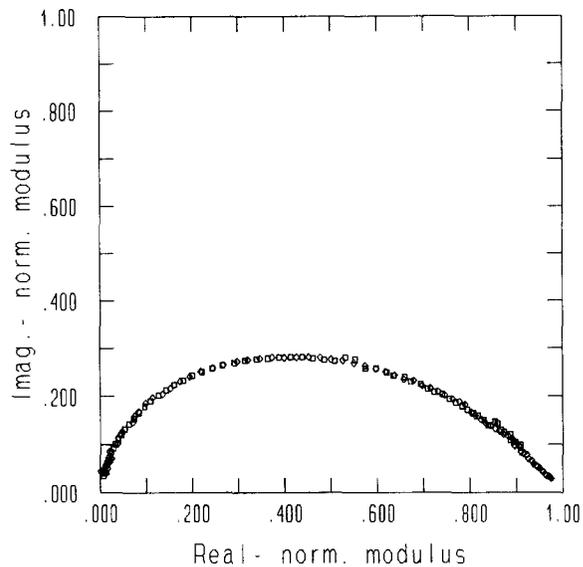


Fig. 2. Shear mechanical and dielectric measurements on silicone oil. The figure shows the normalized shear modulus,  $G_s$ , (10 Hz-60 kHz) at 227.5 K ( $\square$ ) and the inverse electrical susceptibility,  $G_{en}$ , (100 Hz-10 MHz) at 232.5 K ( $\diamond$ ).

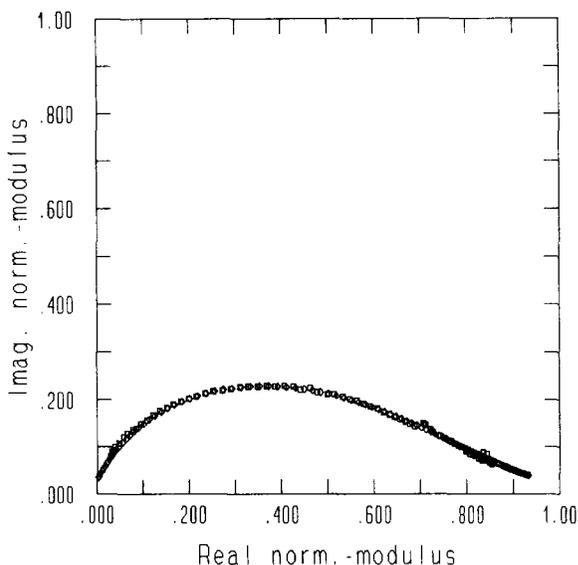


Fig. 3. Shear mechanical and dielectric measurements on 1,3-Butandiol. The figure shows the normalized shear modulus,  $G_s$ , (10 Hz-60 kHz) at 190.0 K ( $\square$ ) and the inverse electrical susceptibility,  $G_{en}$ , (10 Hz-10 MHz) at 194.0 K ( $\diamond$ ).

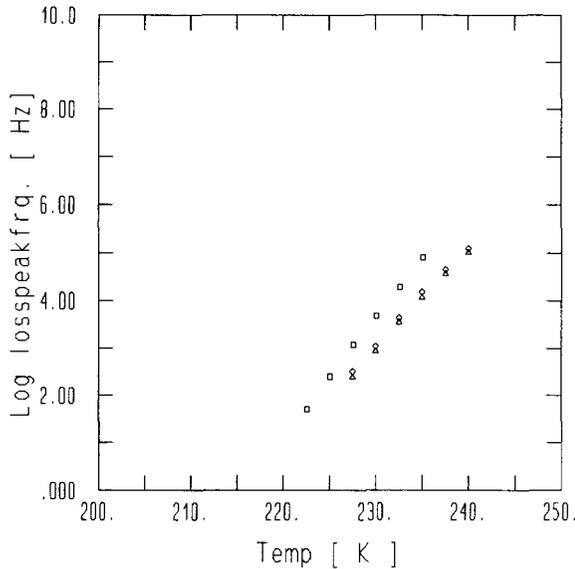


Fig. 4. Loss peak frequencies as function of temperature of silicone oil for the shear mechanical modulus,  $G_s$  ( $\square$ ), the dielectrical modulus,  $G_e$  ( $\diamond$ ), and the dielectrical susceptibility,  $\chi$  ( $\triangle$ ).

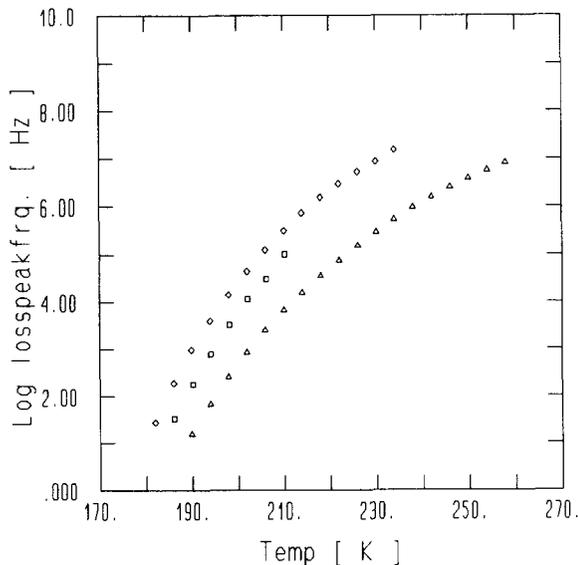


Fig. 5. Loss peak frequencies as function of temperature of 1,3-Butandiol for the shear mechanical modulus,  $G_s$  ( $\square$ ), the dielectrical modulus,  $G_e$  ( $\diamond$ ) and the dielectrical susceptibility,  $\chi$  ( $\triangle$ ).

The uncertainty on a log scale is 0.1 for  $G_s$  and 0.001 for  $G_e$ . Figs. 4 and 5 show  $\log(f_p)$  for  $G_s$ ,  $G_e$  and  $\chi$ . For the silicone oil, the loss peak frequencies for  $G_e$  and  $\chi$  are nearly identical (because of the small relaxation strength). For 1,3-Butandiol, the loss peak frequency for  $G_e$  is 1.8 decade and 1.4 decade above that of  $\chi$ , at low and high temperatures, respectively. The shift in  $\log(f_p)$  between  $G_s$  and  $G_e$  is 0.6 and  $-0.7$  for silicone oil and 1,3-Butandiol, respectively, independent of temperature. If these shifts were caused by a systematic temperature shift, the latter would be 2 K and  $-2.5$  K, respectively, for the two liquids, which means a factor of 10 larger than the experimental error.

#### 4. Discussion

In Eq. (4), the left hand side represents the normalized relaxational part of  $\epsilon$ . This function is shown in Fig. 1 ( $\triangle$ ,  $\chi_n$ ). If the right hand side of Eq. (4) were to be normalized in the same way, then  $K$  would become infinite, which is unphysical. The best fit to Eq. (4) is obtained by  $K = 2 \times 10^{-8} \text{ Pa}^{-1}$  for 1,3-Butandiol and  $K = 4 \times 10^{-9} \text{ Pa}^{-1}$  for silicone oil. Since the fits to Eq. (4) (not shown) are qualitatively poorer than a direct comparison of  $G_{en}$  and  $G_{sn}$  as seen in Figs. 2 and 3, we maintain the idea that  $G_{en}$  and  $G_{sn}$  should be correlated. For clarity, each relaxation function is shown for one temperature only. The difference in temperature between  $G_{sn}$  and  $G_{en}$  has been chosen in order to compensate both for the shift in loss-peak frequency between  $G_s$  and  $G_e$  and for the difference in the applied frequency interval between the  $G_s$  and  $G_e$  measurements. We have found the temperature-timescale principle held at the temperatures in consideration and in both types of measurement. Thus the difference in temperature does not affect the shape of the shown relaxation functions.

In order to relate  $G_e$  and  $G_s$ , we can invert Eq. (3) and obtain

$$G_e(\omega) = (1/4\pi n \alpha(\omega)) - \frac{1}{3}. \quad (5)$$

As seen from Eq. (5),  $G_e$  and not  $M$  is additive in the microscopic modulus,  $\alpha^{-1}$ , in Clausius-Mossotti approximation. If we generalize Debye's 1. theory

putting  $\eta = -G_s/i\omega$  and ignore the atomic polarization, we obtain from Eqs. (1), (2) and (5)

$$G_e(\omega) = G_0 + KG_s(\omega),$$

where

$$G_0 = \frac{3k_B T}{4\pi n \mu^2} - \frac{1}{3}, \quad K = \frac{6R^3}{n\mu^2}. \quad (6)$$

From Eq. (6) one has  $G_{en} = G_{sn}$ , which is in good agreement with Figs. 2 and 3. On the other hand, Eq. (6) disagrees with Figs. 4 and 5, since the loss peak frequencies of  $G_e$  and  $G_s$  from Eq. (6) should be identical.

It has been shown that the shift in loss peak frequencies between  $G_e$  and  $\chi$  is temperature-dependent, and that the loss peak frequency of  $G_s$  within experimental error follows that of  $G_e$  but is shifted to higher and lower frequencies for liquids with low and high low relaxation strength, respectively. It should be noted that, by adding a constant  $\alpha_a$  (which could be an atomic polarizability) to  $\chi(\omega)$ , the two loss peak frequencies in this way could be adjusted to coalescence. This procedure creates two problems, namely, (i)  $\alpha_a$  would become negative for 1, 3-Butandiol and (ii) the shapes of  $G_{en}$  and  $G_{sn}$  would differ significantly both for 1, 3-Butandiol and the silicone oil. Further measurements on more liquids are in progress in order to study whether the

found identity between the shapes of  $G_e$  and  $G_s$  is of a general nature.

## 5. Conclusion

Two liquids have been studied, one with a strong relaxation strength (1, 3-Butandiol) and one with a small relaxation strength) a silicone oil). The normalized relaxational part of the shear mechanical modulus,  $G_s(\omega)$ , and the dielectrical modulus,  $G_e(\omega)$ , defined as the inverse susceptibility, are identical in shape, but with different loss peak frequencies. The ratio of the loss peak frequencies of  $G_s$  and  $G_e$  are independent of temperature, and that of  $G_s$  is higher or lower than that of  $G_e$  in the case of small or strong relaxational strength respectively.

## References

- [1] P.B. Macedo, C.T. Moynihan and R. Bose, *Phys. Chem. Glasses* 13 (1972) 171.
- [2] J.C. Dyre, *J. Non-Cryst. Solids* 135 (1991) 219.
- [3] P. Debye, *Polar Molecules* (Dover, New York, 1929).
- [4] E.A. DiMarzio and M. Bishop, *J. Chem. Phys.* 60 (1974) 3802.
- [5] T. Christensen and N.B. Olsen, to be published.