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Quasistatic measurements of the frequency-dependent bulk and shear modulus of supercooled liquids

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Abstract

By using two newly developed experimental methods, the adiabatic bulk modulus, K_s , and the shear modulus, G , of 1,2,6-hexanetriol have been measured. In the frequency range 15 Hz–15 kHz and temperature range 202–230 K, the glass transition appears as a frequency dependence of K_s and G . It is found that G and the relaxational part, K_r , of K_s have an identical frequency dependence, while the ratio of the loss peak frequencies of G relative to K_r is 1.8.

1. Introduction

Thorough studies of the viscoelastic properties of some supercooled liquids at the glass transition have earlier been carried out in the ultrasonic regime [1,2]. Especially for a series of alcohols including 1,2,6-hexanetriol, a comparison of the distribution of relaxation times describing shear and bulk relaxation was made [3]. The aim of this work is to do this comparison in the sonic regime, where we are in the position to measure the adiabatic bulk modulus, K_s , and the shear modulus, G , independently.

2. Experimental procedures

The experimental methods [4] are both based on piezoelectrical transducers. In either case, the

mechanical interaction between the transducer and the liquid modifies the electrical capacitance of the transducer in a calculable way. Thus, by measuring an electrical impedance, one can deduce the mechanical impedance of the liquid. The two devices have different geometry and can be used for determining the bulk and the shear modulus, respectively. The transducers were operated in the quasistatic regime below 15 kHz, that is the sample size is much smaller than the corresponding acoustical wavelength. The lower limit (15 Hz) was set by the HP 4192A impedance analyzer, which was used in the measurements. The uncertainty on G is 10% including systematic errors, but only 2% in the relative variation of G with frequency. The uncertainty on K is 2%. It is a crucial point in the comparison of shear and bulk modulus that the two measurements were carried out on the same liquid in the same cryostat. Moreover, 1,2,6-hexanetriol is not as hygroscopic as some of the other alcohols, e.g., glycerol, so reproducible results can be obtained.

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3. Results

The real parts of K_s and G as a function of the logarithm of the frequency at several temperatures are shown in Fig. 1 and 2, respectively. There are 20 datapoints per decade at each temperature. The imaginary parts of K_s and G at 218 K are shown together in Fig. 3. It is seen that the loss peak frequency, $f_{p,G}$, is higher than the loss peak frequency, $f_{p,K}$, of K_s , and it is found that $f_{p,G}/f_{p,K}$ is constantly 1.8 in the interval 214-222 K, where the loss peaks are within the experimental frequency range. The normalized relaxation functions are introduced as $G_n = G/G_\infty$ and $K_n = (K_s - K_0)/(K_\infty - K_0)$. The limiting moduli are temperature-dependent and given by: $G_\infty = 7.10 - 2.1 \times 10^{-2} T$; $K_0 = 8.97 - 1.7 \times 10^{-2} T$; $K_\infty = 14.29 - 2.2 \times 10^{-2} T$, with temperatures in K and moduli in GPa. The imaginary versus the real part of G_n and K_n is shown in an Argand plot in Fig. 4. The three decades of frequencies cover only a part of the wide relaxation spectrum of 1,2,6-hexanetriol. Therefore datapoints at the two temperatures 206 and 218 K

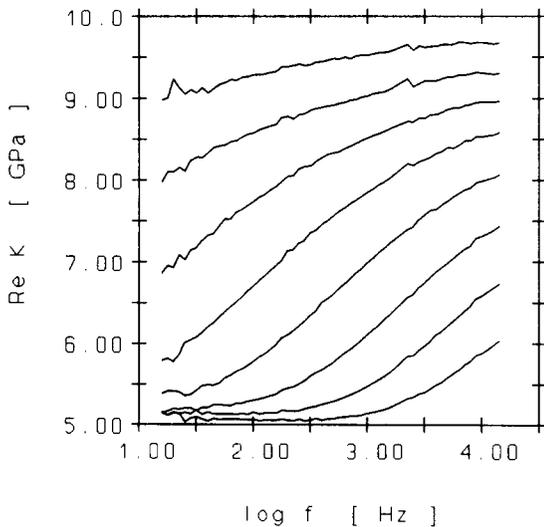


Fig. 1. The real part of bulk modulus, K_s , as a function of the logarithm of the frequency, f . The solid lines are drawn between datapoints (20 per decade) belonging to the same temperature. The curves are drawn in ascending order as the temperature is lowered from 230 K to 202 K in steps of 4 K.

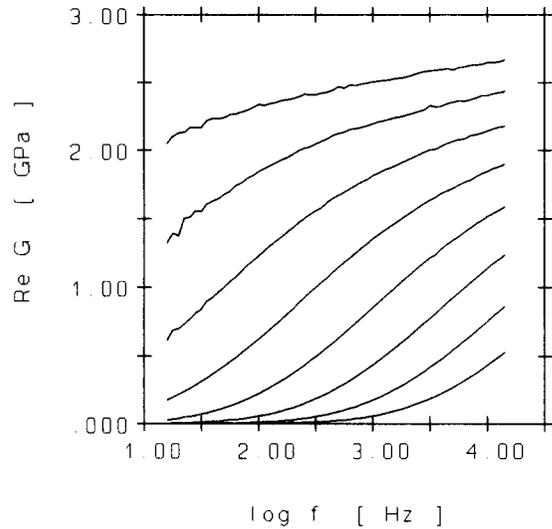


Fig. 2. The real part of shear modulus, G , under the same conditions as in Fig. 1.

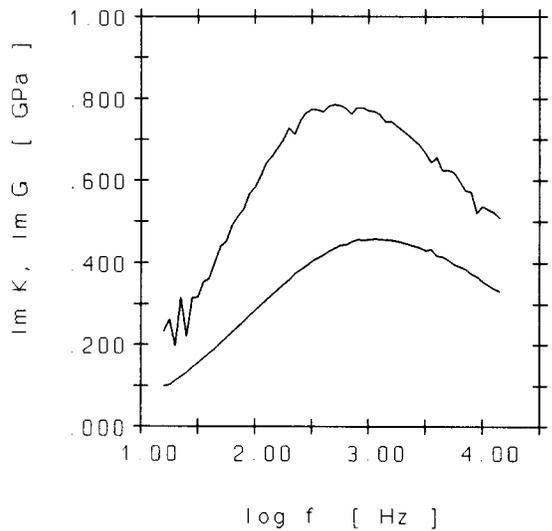


Fig. 3. The imaginary part of K_s (upper curve) and G (lower curve) at 218 K. The loss peak frequencies are not coincident.

are put together on the Argand diagram forming a masterplot.

4. Discussion

It is clearly seen in Fig. 4 that K_n and G_n have identical shapes within the uncertainty. This is not

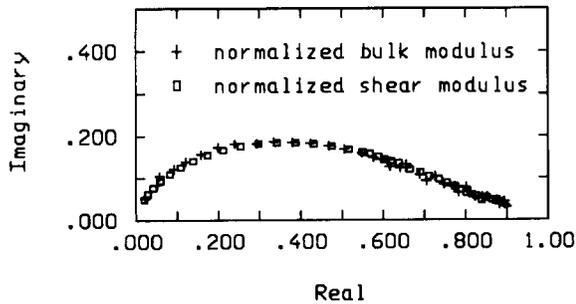


Fig. 4. The normalized bulk modulus and normalized shear modulus in the same Argand diagram.

necessary contradictory to the earlier mentioned fact that the loss peak frequencies are different. For example, in the simplest rheological models, where G_n and K_n are described by Maxwell elements, the equality of the shear and bulk viscosity infers the non-equality of the shear and bulk relaxation times. This is so because the characteristic moduli are different in the two cases. In this example, however, $G_\infty < K_\infty - K_0$ gives $f_{p,G} < f_{p,K}$ contrary to what is observed.

Meister et al. [3] found differences in the shear and bulk distribution of relaxation times for all of the four liquids studied. In the case of 1,2,6-hexanetriol, the shear relaxation was described by a sum of a single relaxation time and a Cole–Davidson distribution with $\beta = 0.32$. The bulk relaxation

was given by a Cole–Davidson distribution with $\beta = 0.24$. However these results depended on a reduction of data using the time–temperature superposition principle, since data could only be found at four different frequencies. Moreover, K_s was only indirectly found via the longitudinal modulus. It is questionable whether the two distributions really are different when the uncertainty in the data reduction is taken into account. In our comparison of shear and bulk relaxation, a direct comparison of measured data is done. We have not tried to fit to a distribution of relaxation times.

5. Conclusion

The direct measurements of the bulk and the shear modulus of 1,2,6-hexanetriol in a continuous frequency range over 3 decades have shown that except for a proportional shift in the frequency, the relaxational parts of G and K_s are proportional.

References

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