

THE FREQUENCY DEPENDENCE OF THE SPECIFIC HEAT AT THE GLASS TRANSITION

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**RESUME** - L'influence de la fréquence du courant électrique de chauffage par effet Joule sur la chaleur spécifique a été étudiée au voisinage de la transition vitreuse du glycérol. Une équivalence temps-température est proposée, le temps de relaxation moyen correspondant à une énergie d'activation de  $2,1 \cdot 10^4$  K. A la limite des hautes fréquences,  $C - C_\infty$  décroît suivant une loi de puissance en 0,28.

**ABSTRACT** - The frequency dependence of the specific heat of glycerol at the glass transition has been measured. A time-temperature equivalence is found - the mean relaxation time having an activation temperature of  $2.1 \cdot 10^4$  K. In the high frequency limit  $c - c_\infty$  decays as a power law with exponent 0.28

The glass transition shows up in various thermodynamic responses such as the specific heat  $c_p$  /1/. When  $c_p$  is measured at a certain cooling rate the glass transition temperature  $T_g$  is found at the "soft discontinuity" in  $c_p(T)$ .  $T_g$  is dependent of the cooling rate, being higher at fast cooling than at slow cooling. Furthermore, hysteresis effects are seen, i.e. cooling and heating gives different curves  $c_p(T)$ , see fig. 1 taken from /2/.

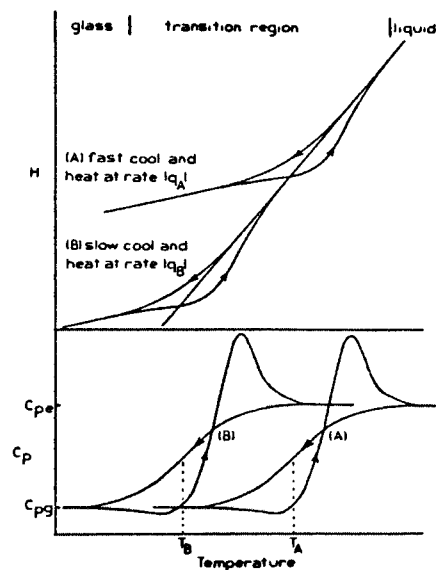


Fig. 1 - Enthalpy and heat capacity vs. temperature plots for a glass cooled and then reheated through the transition region at different rates.

The physical picture of the glass transition is that near  $T_g$  some degrees of freedom are so slowly approaching equilibrium (times exceeding the duration of the experiment), that they cease to contribute to  $c_p$ .

Usually the enthalpy relaxation near  $T_g$  is measured in the time domain. In this work we have considered the frequency domain.

Doing linear nonequilibrium thermodynamics, we apply an AC-heating current  $I_0 e^{i\omega t}$ , small enough for the temperature response  $T_0 e^{i(\omega t + \phi)}$ , to be linear. The heat impedance is defined as  $Z = T_0 e^{i\phi} / Q_0$  and the complex heat capacity becomes  $c = 1/i\omega Z$ .

In a substance with structural relaxation  $c$  will have a nonvanishing imaginary part. As for more commonly considered susceptibilities,  $\text{Im}(c)$  is proportional to the entropy production during a cycle due to irreversible processes.

AC-temperature calorimetry is a technique known to have the advantage of a high signal-to-noise ratio /3/, and has been used to determine critical exponents of equilibrium phase transitions /4/, where  $c_p$  is independent of  $\omega$ . It turns out to be a powerful method for a relaxing heat capacity allso.

EXPERIMENTAL

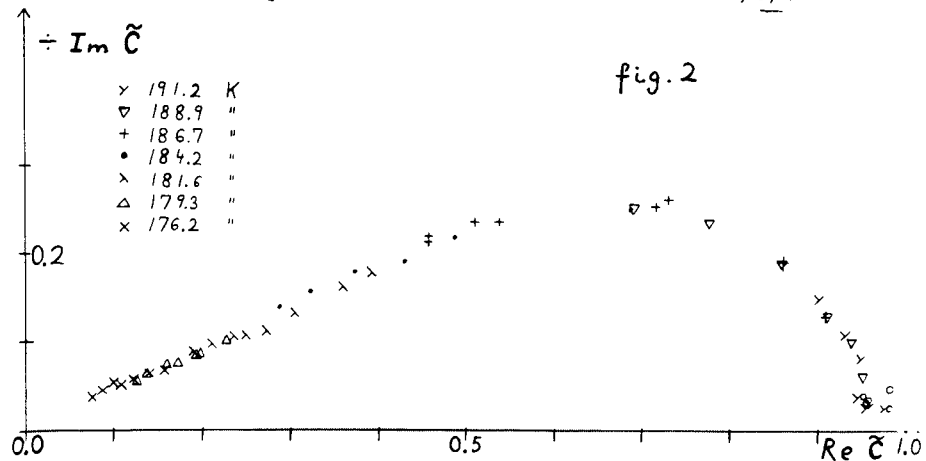
$c(\omega)$  has been measured for glycerol. 130 mg glycerol was put between two concentric alumina cylinders 0.3 mm apart. The heat current were send into the liquid at the inner cylinder, and the temperature measured at the outer cylinder. The frequency range was 2,4 mHz to 35 mHz, - the lower time limit set by the heat diffusion time in the sample and the upper time limit by the patience of the experimentalist. The temperature was measured every half second by a computer, and through a Fourier analysis the amplitude and phase were determined.

REDUCED DATA

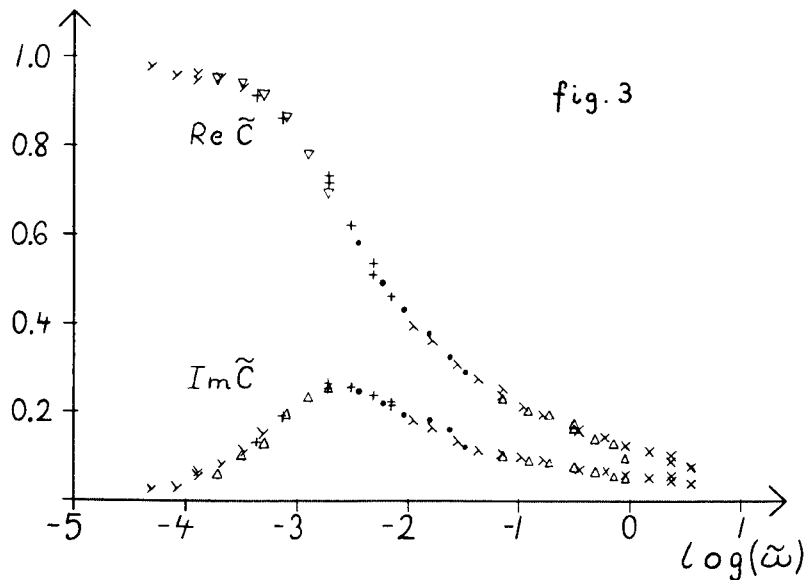
After subtracting the background admittance consisting of container-capacity and heat conductivity to temperature bath, the data were subjected to the following procedure. The liquid heat capacity  $c_\infty(T)$  and the glass heat capacity  $c_0(T)$  were extrapolated into the transition region and  $c_p$  normalized to

$$\tilde{c}(\omega, T) = \frac{c_p(\omega, T) - c_\infty(T)}{c_0(T) - c_\infty(T)}$$

The real and imaginary part of  $\tilde{c}$  is presented in fig. 2 in a Cole-Cole plot. The segments belonging to different temperatures fall on the same mastercurve indicating that the principle of corresponding states (time - temperature equivalence) is valid; that is  $\tilde{c}$  is of the form  $\tilde{c}(\omega \cdot \tau(T))$ ,  $\tau(T)$  being a kind of mean relaxation time /5/.



In the high frequency end the Cole-Cole plot is a straight line which shows  $\tilde{c}(\tilde{\omega}) \propto (i\tilde{\omega})^{-\beta}$  ( $= \tilde{\omega}^{-\beta} e^{-i\beta\pi/2}$ ) for  $\omega \rightarrow \infty$ . The angle of this line with the  $\text{Re } \tilde{c}(\tilde{\omega})$  axis is  $-\beta\pi/2$ .  $\beta$  is found to be 0,28. The time - temperature equivalence have now been used to make the mastercurve of fig. 3. The various segments of  $\tilde{c}(\tilde{\omega})$  measured at different temperatures were displaced along the  $\log(\tilde{\omega})$  axis to form a single curve. The displacements followed an Arrhenius law  $\tau \propto \exp(\frac{A}{T})$  with  $A = 2.1 \times 10^4$  K. At  $T = 184.2$  the  $\tilde{\omega}$ -axis can be read in Hz.



The intention of future work is to relate  $\tilde{c}(\tilde{\omega})$  to other known responsefunctions at the glass transition.

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#### REFERENCES

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