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1999 J. Phys.: Condens. Matter 11 L451

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## LETTER TO THE EDITOR

**The quasi-critical behaviour of electric conductivity in glass-forming liquids**

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Received 17 August 1999, in final form 7 September 1999

**Abstract.** Results are presented of temperature studies of electric conductivity, for a few frequencies from 100 Hz to 100 kHz, in liquid glass-formers: dibutyl phthalate, glycerol and salol. It has been shown that the analysis of experimental data similar to that applied in non-critical liquid mixtures of limited miscibility may offer a relatively precise and simple estimation of the mode-coupling critical temperature ( $T_C$ ) and exponent ( $\gamma$ ). Preliminary pressure studies point to the possibility of isomorphic behaviour for the temperature and the pressure paths approaching the mode-coupling critical point.

One of the most important predictions of mode-coupling theory (MCT) for glass-forming liquids is the appearance of the critical temperature  $T_C$ , located well above the glass temperature  $T_g$ , at which some physical properties exhibit a power-type divergence (Cummins *et al* 1997, Cummins 1999, Goetze and Sjoegren 1992, Goetze 1999, Knob *et al* 1997, Shoenhals *et al* 1993, Taborek *et al* 1986)

$$\tau^{-1}, D, \eta \propto (T - T_C)^\gamma \quad (1)$$

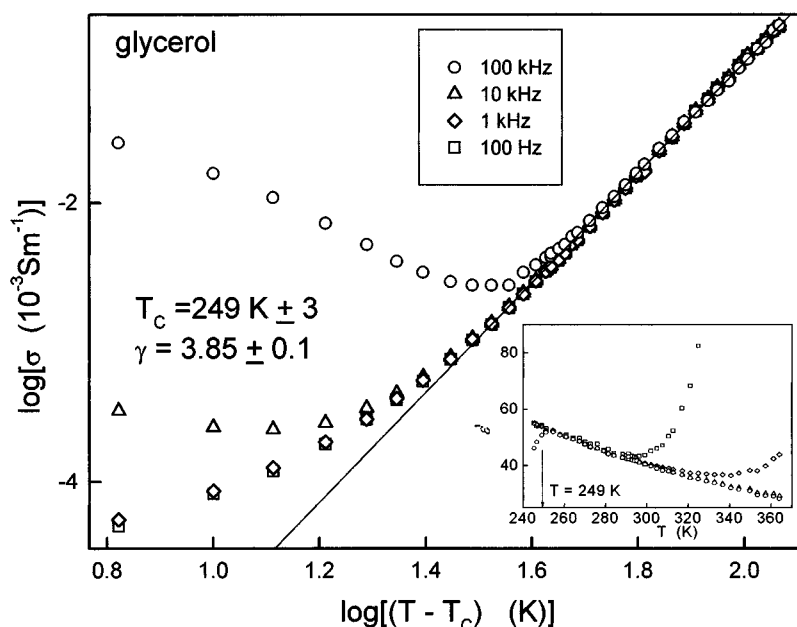
where  $\tau$  is the primary ( $\alpha$ ) relaxation time,  $D$  is the diffusion constant and  $\eta$  the viscosity. The same type of behaviour is observed on approaching the continuous or weakly discontinuous phase transitions in liquids. However, in such a case power exponents are universal quantities whose values depend only on the dimensionality of the system ( $d$ ), dimensionality of the order ( $n$ ) parameter and the range of interaction. Additionally, the critical exponents describing different physical magnitudes are interrelated by scaling laws and only two of them are independent (Anisimov 1992). Such universality has not yet been found in glass-formers. The exponent  $\gamma = 2-4$  and its value depends on the material tested (Cummins *et al* 1997, Cummins 1999, Goetze and Sjoegren 1992, Goetze 1999, Taborek *et al* 1986).

The application of relation (1) makes it possible to determine the mode-coupling critical temperature on the border of ergodic and non-ergodic behaviour (Goetze and Sjoegren 1992, Goetze 1999). The practical tests on the predictions of MCT, including relation (1), were spawned due to sophisticated experimental techniques such as quasi-elastic neutron scattering (Goetze and Sjoegren 1992, Goetze 1999), dynamic light scattering (Cummins *et al* 1997, Cummins 1999), high-frequency dielectric spectroscopy (Goetze and Sjoegren 1992, Goetze 1999, Shoenhals *et al* 1993) and shear viscosity (Goetze and Sjoegren 1992, Goetze 1999, Taborek *et al* 1986). It is worth noting that the mode-coupling critical temperature had to be estimated based on data remote from  $T_C$ . Similar extrapolation is known in non-critical

binary solutions of limited miscibility to determine the position of the spinodal curve from measurements in the homogeneous region, applying so-called pseudospinodal hypothesis (Chu *et al* 1969):

$$\eta_C, D_C, I_L, \varepsilon_{NDE} \propto (T - T_{SP})^\phi \quad T > T_B = T_{SP} + \Delta T \quad (2)$$

where  $T_B$  is the temperature of a discontinuous phase transition (the binodal temperature),  $T_{SP}$  is the so-called pseudospinodal temperature and  $\Delta T$  is the measure of the discontinuity of the transitions.  $\eta_C$ ,  $D_C$ ,  $I_L$  and  $\varepsilon_{NDE}$  are ‘critical’ parts of the shear viscosity, the diffusion constant, intensity of the scattered light and nonlinear dielectric effect (NDE), respectively. The value of the universal critical exponent depends on the magnitude tested:  $\phi \approx -0.033$  for  $\eta_C$  (Dega-Dałkowska 1993, Abdulagatov *et al* 1994),  $\phi \approx -1$  for  $D_C$  (Abdulagatov *et al* 1994),  $\phi \approx -1.23$  for  $I_L$  (Chu *et al* 1969) and  $\phi \approx -0.4$  for the NDE (Chrapeć *et al* 1987).



**Figure 1.** Results of electric conductivity measurements for glycerol on a log–log scale as a function of the temperature distance from the mode-coupling critical temperature. The insert in figure 1 shows the temperature dependence of  $\varepsilon'$  in the same ranges of temperature and frequency.

It may be concluded from Chu *et al* (1969) and Chrapeć *et al* (1987) that for  $\Delta T = 1\text{--}2$  K the error of its estimation, as well the error of the exponent  $\phi$ , is about 10%. In glass-forming liquids the ‘discontinuity’, i.e. the distance from  $T_C$  where relation (1) ceases to be valid, is equal to 10–20 K (Goetze and Sjoegren 1992, Shoenhals *et al* 1993). This comparison points to a problem in the experimental method in testing relation (1).

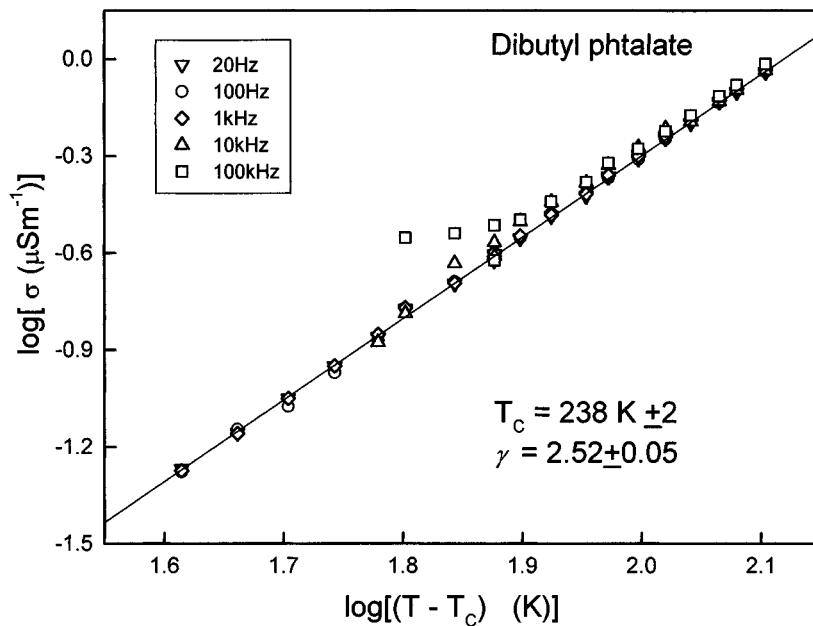
In this paper we report studies of the electric conductivity ( $\sigma$ ) whose results suggest that relation (1) may also be valid for this physical property. Apart from temperature studies, preliminary isothermal pressure studies were also carried out. They were aimed at testing the validity of equation (1) for the pressure path approaching the eventual critical pressure ( $P_C$ ). Measurements were conducted using the Wayne-Kerr 6425 RLC bridge. For temperature studies the sample was placed in a flat-parallel capacitor (gap 0.1–1 mm, diameter 20 mm) made from Invar (Rzoska *et al* 1988). The temperature was stabilized using a Julabo FP

45HD thermostat with precision  $\pm 0.01$  K. It was measured by means of a platinum resistor (DIN 43 260) placed in one of the capacitor covers and a Keithley 195A multimeter. Pressure studies were carried out using the pressure system described in the author's earlier studies (Drozd-Rzoska 1999).

Figures 1 and 2 show results of conductivity measurements for glycerol and dibutyl phthalate. Data are shown on a log-log scale. The temperature  $T_C$  was optimized until part of the data for all the applied frequencies followed a common straight line in the widest range of temperatures. Figure 3 shows that if  $T_C$  is underestimated the common part of the  $\sigma(T)$  dependences for different frequencies bends down. If  $T_C$  is overestimated the number of measuring points lying on a straight line is significantly smaller than for the optimal fit in figure 1. Hence, for the value of  $T_C$  optimized in this way

$$\sigma(T) \propto (T - T_C)^\gamma \quad \text{for } T > T_x^f \quad (3)$$

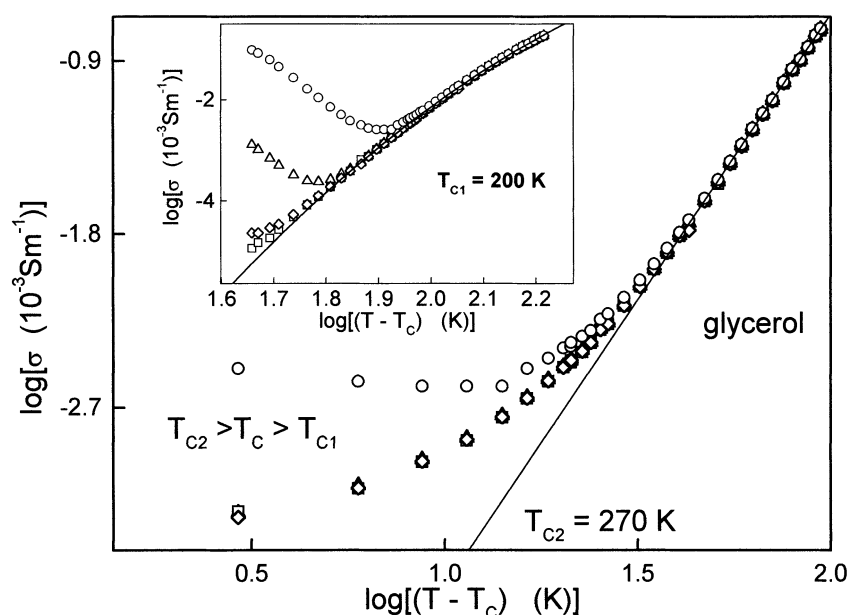
where  $T_x^f$  denotes the temperature at which relation (3) ceases to describe the experimental data for a given frequency.



**Figure 2.** Results of electric conductivity measurements in dibutyl phthalate on a log-log scale as a function of the temperature distance from  $T_C$ .

Table 1 shows the results of fits for dibutyl phthalate and glycerol. It also contains results of tests conducted in salol. The values of  $T_C$  and  $\gamma$  for glycerol and salol are in a good agreement with reference data from the analysis of the temperature evolution of the primary relaxation time. To obtain such data the dielectric function  $\varepsilon^*(f) = \varepsilon'(f) + \varepsilon''(f)$  had to be measured up to  $10^{10}$  Hz. Unfortunately, the authors did not find reference data for dibutyl phthalate.

The insert in figure 1 shows a typical dependence of the dielectric permittivity  $\varepsilon'$  in the tested range of temperatures. Concerning this quantity, the critical-like behaviour discussed above seems to be absent. For higher temperatures and lower frequencies the ionic polarization boost  $\varepsilon'$  towards large values. On cooling, for the highest tested frequency the influence of relaxation processes starts to be visible. The nearly linear part of the  $\varepsilon'(T)$  dependence can



**Figure 3.** The behaviour of electric conductivity in glycerol for the over- and the underestimated value of  $T_C$ .

**Table 1.** Values of temperatures  $T_C$  and exponents  $\gamma$  obtained in the analysis of electric conductivity data. Asterisks denote reference data from Shoenhals *et al* (1993).

Parameter	Liquid		
	Glycerol	Dibutyl phthalate	Salol
$T_C$ (K)	$249 \pm 1$ $248.8$ (*)	$238 \pm 2$	$270 \pm 4$ $267.7$ (*)
$\gamma$	$3.85 \pm 0.15$ $3.65$ (*)	$2.52 \pm 0.05$	$2.04 \pm 0.2$ $2.25$ (*)

be associated with the static domain. The temperature dependence of static  $\varepsilon'(T)$  may be due to the existence of molecular associates. The rise of temperature may disturb them and hence decrease the value of  $\varepsilon'(T)$  (Chełkowski 1980).

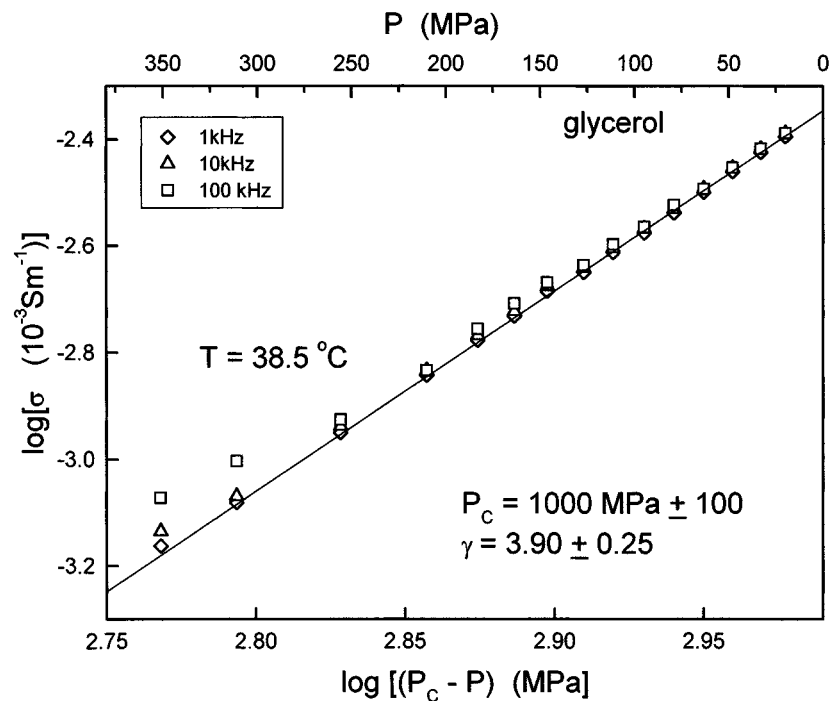
Figure 4 shows preliminary results of isothermal pressure measurements in glycerol. The same method of analysis yielded

$$\sigma(P) \propto (P_C - P)^\gamma \quad \text{for } P < P_x^f \quad (4)$$

with  $\gamma \approx 3.9$  and  $P_C \approx 1000$  MPa.

Within the limit of the experimental error the exponent  $\gamma$  is the same for the isothermal pressure and isobaric temperature paths. Such behaviour confirms that the postulate of isomorphism of critical phenomena is valid for the mode coupling critical point in glass-formers, as in the case of weakly-discontinuous phase transitions (Anisimov 1999, Rzoska *et al* 1997, Drozd-Rzoska 1999).

In conclusion, the results presented above have shown the possibility of applying electric conductivity studies to test some predictions of the MCT model. It is worth noting, in particular, that the method is relatively simple experimentally in comparison with other methods



**Figure 4.** Results of isothermal, pressure measurements of electric conductivity in glycerol on a log–log scale as a function of temperature distance from the mode-coupling critical pressure.

mentioned above, and it involves experimentally convenient frequencies. The method of analysis of the experimental data is analogous to that applied in the pseudospinodal analysis. The proper estimation of  $T_C$  and  $\gamma$  is supported by the possibility of using a large number of experimental points. The validity of relation (3) may be a consequence of the Einstein–Nernst (Goetz and Sjoegren 1992) relation  $\sigma/D = ne^2/kT$ . The preliminary pressure test shows that for the mode-coupling critical point in glass-formers a ‘critical isomorphism’ for the temperature and the pressure ‘pretransitional’ behaviour may take place. The results presented, together with other experimental tests of relation (1) show that the critical-like behaviour takes place remote from the ‘critical point’, also in the ‘ordinary’ state of a liquid. This suggests that the MCT ‘critical point’ may be determined for any liquid.

This research was supported by the State Committee for Scientific Research, Poland (Komitet Badań Naukowych, Polska), grant No 2 P03B 030 12.

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