

Excess wing and high frequency dynamics in plastic crystals

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ABSTRACT

Results from broadband dielectric spectroscopy on plastic crystals are summarized with special emphasis on cyclo-octanol. Further experimental evidence is provided that the apparent excess wing suspected to be present in this material is due to secondary relaxations. In the loss spectra obtained for three other plastic crystals the excess wing is absent. The scaling procedure, demonstrated to collapse dielectric spectra of structural glass formers onto one master curve, does not work for plastic crystals.

§1. INTRODUCTION

In the dynamic response of glass-forming materials a variety of dynamic processes with different timescales shows up. Due to the extremely broad dynamic range accessible, dielectric spectroscopy is an ideal tool for the investigation of these processes. In plastic crystals (PCs), the centres of mass of the molecules form a regular crystalline lattice but the molecules are dynamically disordered with respect to the orientational degrees of freedom. PCs are often considered as model systems for structural glass formers (SGFs), but are much simpler to treat in theoretical approaches. Indeed dielectric spectra of dipolar PCs show similar characteristics as those of SGFs: in the frequency dependence of the dielectric loss, $\epsilon''(\nu)$, the α -relaxation peak shows up, slowing down dramatically when the glass temperature T_g is approached. Its spectral shape usually is described by phenomenological functions as, e.g., the Cole–Davidson (CD) function (Davidson and Cole 1951). However, for SGFs at frequencies about 2–3 decades above the peak frequency ν_p , deviations from these empirical functions show up that can be described by a second power law, $\epsilon'' \sim \nu^{-b}$, in addition to the first power law, $\epsilon'' \sim \nu^{-\beta}$ ($\beta > b$), observed above ν_p (Dixon *et al.* 1990, Hofmann *et al.* 1994, Lunkenheimer *et al.* 1996b, Leheny and Nagel 1997). This excess wing was noted a long time ago (Davidson and Cole 1951), and is a universal feature of glass-forming liquids, at least for all systems where secondary relaxation processes are absent. As yet there is no commonly accepted explanation of the microscopic origin of the excess wing in glass-forming liquids, although there are some theoretical approaches that are able to describe the wing at least partly (Chamberlin 1993, Tarjus *et al.* 1997). In some glass-formers one or more additional loss peaks show up at frequencies above that of the α -peak. Such secondary processes, termed β -processes, can often be ascribed to intramolecular degrees of freedom. However, more fundamental reasons for their occurrence have been proposed (Johari and Goldstein 1970, Ngai 1998). It was

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argued that the excess wing may be a β -relaxation peak, hidden under the dominating α -peak (Hofmann *et al.* 1994, Ngai 1998). However, commonly the excess wing and possible β -relaxations are considered as different phenomena, a notion which will be followed in the course of the present paper.

In the GHz–THz frequency regime a minimum shows up in the loss spectra of SGFs and finally another loss peak appears at some THz, the microscopic or boson peak. The minimum region is of special interest, because here contributions from fast processes are found (see, e.g. Lunkenheimer *et al.* (1996a, 1997)) as, e.g., expected within the framework of mode coupling theory (MCT) of glass transitions (Götze and Sjögren 1992). In PCs, reports on the excess wing and the minimum region are scarce. In the present work we will give a brief overview of our dielectric results on PCs, concentrating on the question of the presence of the excess wing and of fast processes in the minimum region in these materials. Especially, further evidence will be provided that in cyclo-octanol (c-OCT), which was considered as a major example for the presence of an excess wing in PCs (Leslie-Pelecky and Birge 1994, Menon and Nagel 1995, Leheny *et al.* 1996), the observed deviations from a single power law at $\nu > \nu_p$ are completely due to secondary relaxations (Brand *et al.* 1997).

§2. RESULTS AND DISCUSSION

Figure 1 shows $\varepsilon''(\nu)$ of cyclo-octanol for various temperatures over the whole frequency range investigated so far. For details on the variety of techniques used to obtain these broadband dielectric data, the reader is referred to previous publications (e.g. Schneider *et al.* (1999)). The spectra are dominated by the typical α -peaks shifting through the frequency window with temperature. They can be fitted

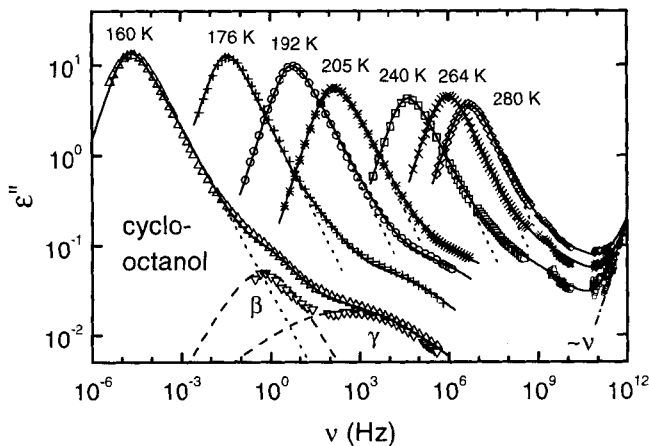


Figure 1. Frequency dependence of the dielectric loss in the PC ($T \geq 240$ K) and the super-cooled PC phase ($T \leq 205$ K) of c-OCT. The dotted lines are fits of the peak region with the CD function. In addition, a curve obtained at 160 K in the orientationally ordered phase is shown (down triangles). The dashed lines indicate a description of the β - and γ -relaxation peaks with two CC curves. The solid lines for $T \leq 192$ K are calculated from the sum of two CC curves and the CD curve describing the α -peak (see text). For $T \geq 205$ K only the sum of a CD and one CC curve was used. The parameters for the CC functions were partly fixed as described in the text. In addition, for $T \geq 240$ K a linear increase was added to take account of the high frequency minimum. The dash-dotted line indicates a linear increase at the lowest temperature.

satisfactorily with the empirical CD function (dotted lines). When cooled slowly, c-OCT exhibits a transition from a phase with fast and isotropic reorientations of the molecules to a (partly) orientationally ordered state at 265 K (Shablakh *et al.* 1983, Anderson and Ross 1990). The α -relaxation observed in the disordered state is absent in this ordered state, i.e., the molecules have ordered with respect to their dipolar active degrees of freedom. At 220 K a further, very slow transition to a completely ordered state is reported (Anderson and Ross 1990). Both transitions can be supercooled using cooling rates of $>5 \text{ K min}^{-1}$. In figure 1 the curves below 205 K have been measured in the supercooled state while the data above 240 K belong to the plastic (dynamically disordered) phase. Between 200 K and 240 K the samples exhibit a time-dependent transition to the ordered phases (figure 2), so it was not possible to obtain reliable results for this temperature range. The reduced peak heights of the 205 K and 240 K curves in figure 1 indicate that the sample was already partly orientationally ordered at these temperatures.

At frequencies 2–3 decades above ν_p , deviations from the CD fits show up that resemble the excess wing known from SGFs. Indeed, based on dielectric measurements of c-OCT at frequencies up to 10 kHz, it was argued that the excess wing is present also in PCs (Leslie-Pelecky and Birge 1994) which would indicate that it is a universal feature of disordered systems in general, regardless of the nature of the disorder. However, from an inspection of figure 1, especially at low temperatures, the presence of two secondary relaxation features (β - and γ -relaxation) can be suspected. In figure 2 loss spectra for different times after quickly ($>10 \text{ K min}^{-1}$) cooling the sample to 213 K are shown. The α -peak intensity successively diminishes when the sample orders orientationally. After some hours the α -peak has almost vanished and the presence of β - and γ -relaxation peaks (at about 3 kHz and 1 MHz, respectively) is revealed. Obviously the β - and γ -relaxations are connected with intramolecular degrees of freedom which still are present in the orientationally ordered phase. Indeed a variety of different molecular conformations exists in c-OCT (Brand *et al.* 1997).

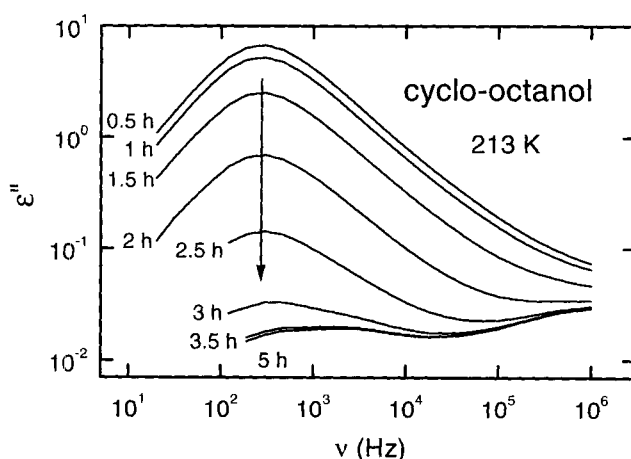


Figure 2. Loss curves of c-OCT obtained at different times after the sample was cooled rapidly to 213 K. With increasing orientational order the α -peak diminishes and the β - and γ -peaks become visible. After 5 h a small remainder of the α -peak is still present at about 300 Hz.

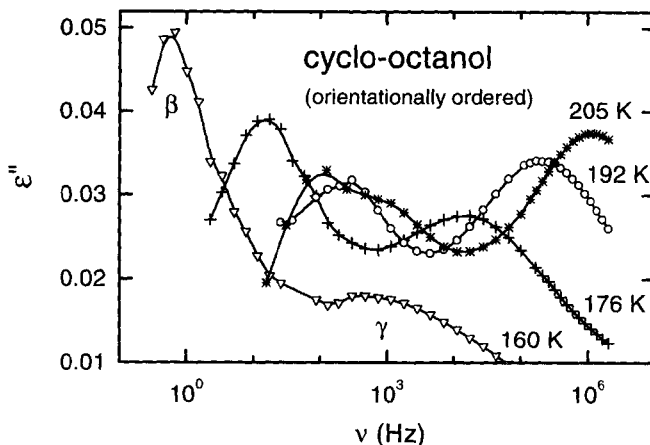


Figure 3. Loss curves of c-OCT in the orientationally ordered phase for various temperatures. The phase was reached after keeping the sample at 230 K for 24 h. The lines are drawn as a guide to the eye.

In figure 3 loss spectra obtained at various temperatures in the orientationally ordered state (reached after waiting for 24 h at 230 K) are shown. Well developed β - and γ -relaxation peaks are seen shifting to higher frequencies with increasing temperature. At 205 K remainders of the α -peak are still present. The peak positions, which give an estimate for the inverse relaxation times, follow a thermally activated behaviour (Brand *et al.* 1997). They are located just in the region of the apparent excess wing seen in figure 1. To demonstrate this more clearly, in figure 1 the 160 K curve obtained in the orientationally ordered state is included. The dashed lines have been calculated using the empirical Cole–Cole (CC) function (Cole and Cole 1941) which is usually used for the description of secondary relaxations. The solid line is the sum of these curves and the CD curve describing the α -peak. In this way a remarkably good fit of the data over 11 decades of frequency is possible. The solid lines for higher temperatures have been calculated using the same ansatz. For $T < 205$ K the β - and γ -relaxation times were fixed at the values determined from the peak positions in the ordered phase (figure 3). For higher temperatures the γ -relaxation times have been fixed at the values determined from an extrapolation of the thermally activated behaviour seen at lower temperatures (Brand *et al.* 1997). With increasing temperature, the β -relaxation starts to merge with the α -relaxation and its amplitude decreases. Therefore for $T \geq 205$ K the sum of a CD with one CC curve only is sufficient for the fits. Overall these results provide clear evidence that the apparent excess wing seen in c-OCT is due to two secondary relaxations.

In the GHz–THz region a minimum in $\varepsilon''(\nu)$ shows up. As shown before (Brand *et al.* 1997), it cannot be fitted assuming a simple superposition of a power law decrease for its low frequency wing and a power law increase towards the boson peak, which seems to be present also in PCs (Ramos *et al.* 1997). Instead an additive superposition of the α - and γ -relaxation contributions (see above) with a power law increase, $\varepsilon'' \sim \nu^n$, were used for the calculation of the solid lines in figure 1 at $T \geq 240$ K. Here $n = 1$ was assumed because at the lowest temperature, where contributions from other processes may be negligible, a linear increase shows up. Rather good fits can be obtained in this way, with some minor deviations in the minimum

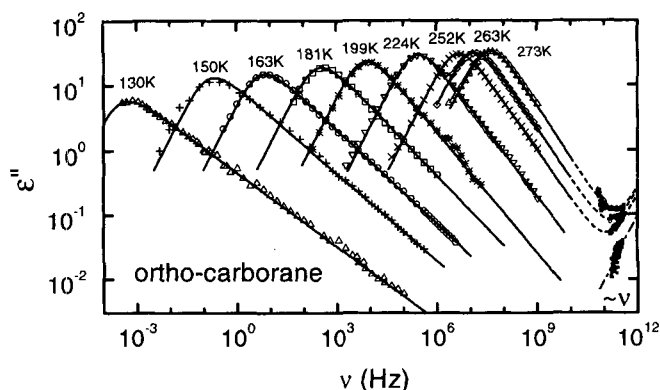


Figure 4. Loss spectra of *ortho*-carborane for various temperatures. The solid lines are fits with the CD function. The dashed lines are calculated from the sum of a power law extending the CD curves and a linear increase. The dash-dotted line indicates a linear increase at the lowest temperature.

region. They may be indicative of additional fast processes in the minimum region as commonly found in SGFs (e.g. Lunkenheimer *et al.* (1996a, 1997)). However, due to the close vicinity of the γ -relaxation to the minimum, it is difficult to make a clear statement concerning this question.

As revealed by the results in c-OCT, it is difficult to obtain information on the excess wing in materials where secondary relaxation processes are present. Therefore we started a series of investigations on PCs with a rigid molecular structure where relaxations due to intramolecular processes can be excluded. So far *ortho*-carborane, *meta*-carborane and 1-cyanoadamantane have been investigated (Brand *et al.* 1999). In figure 4 the loss spectra for *ortho*-carborane are shown for various temperatures. $\varepsilon''(\nu)$ exhibits well developed α -relaxation peaks shifting through the frequency window with temperature. The experimental spectra show no trace of an excess wing and the CD function (solid lines) describes the data perfectly well. For 130 K, even with up to eight decades of frequency above ν_p no significant deviations from the CD fits are seen. Similar behaviour was found also for *meta*-carborane and 1-cyanoadamantane (Brand *et al.* 1999). As seen in figure 4, despite only few data having been collected above GHz, the presence of an $\varepsilon''(\nu)$ minimum is revealed clearly. The dotted lines have been calculated using the sum of two power laws, $\varepsilon'' = c_\beta \nu^\beta + c_n \nu^n$. β was chosen equal to β_{CD} as obtained from the fits of the α -peak with the CD function. For the increase towards the boson peak again $n = 1$ was assumed. The dashed lines in figure 4 are fully consistent with the experimental data, which would imply that, in contrast to the findings in SGFs, in *ortho*-carborane no additional fast processes contribute in the minimum region. More data in this high frequency region have to be collected to clarify this point.

A very interesting empirical finding concerning the spectral forms of the α -peak and the excess wing in SGFs is given by Nagel-scaling (Dixon *et al.* 1990). Nagel and coworkers demonstrated that $\varepsilon''(\nu)$ curves for different temperatures and even for different materials, including the wing, can be scaled onto one master curve by plotting $Y := 1/w \log_{10}[\varepsilon'' \nu_p / (\Delta \varepsilon \nu)]$ versus $X = 1/w(1 + 1/w) \log_{10}(\nu/\nu_p)$. Here w denotes the half-width of the loss peak normalized to that of the Debye peak, ν_p is the peak frequency, and $\Delta \varepsilon$ the relaxation strength. This scaling behaviour strongly

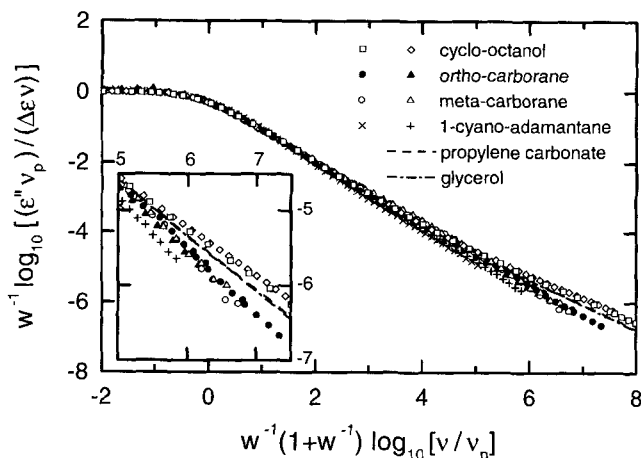


Figure 5. Nagel-plot (Dixon *et al.* 1990) of dielectric loss data on all PCs investigated: *ortho*-carborane (●, 130 K; ▲, 150 K), *meta*-carborane (○, 200 K; △, 210 K), 1-cyano-adamantane (×, 280 K; +, 300 K) and c-OCT (□, 192 K; ◇, 200 K). In addition, two curves for typical SGFs are included which closely follow the master curve found for SGFs (Dixon *et al.* 1990): propylene carbonate (dashed line, 158 K) and glycerol (dash-dotted line, 195 K).

suggests a correlation of α -process and excess wing. In figure 5, a Nagel-scaling plot is shown for all the PCs investigated so far. For clarity reasons, curves for two temperatures only are shown for each material. In addition two curves for the SGFs glycerol and propylene carbonate are shown (Schneider *et al.* 1998, 1999) that closely follow the master curve, found by Nagel and coworkers (Dixon *et al.* 1990). Clearly, Nagel-scaling does not work for the PCs investigated. The curves for the carboranes and 1-cyanoadamantane fall below the master curve which can be ascribed to the absence of the excess wing. By contrast, the curves obtained for c-OCT are located *above* the master curve due to the contributions from the β - and γ -relaxations.

§3. CONCLUSION

In summary, broadband dielectric spectroscopy on a variety of PCs reveals a marked difference from typical spectra of SGFs. The excess wing, which seems to be universally present in SGFs is absent in the PCs investigated. We have provided clear experimental evidence that the apparent excess wing in c-OCT, which until now was considered as main evidence for the presence of the excess wing in PCs (Leslie-Pelecky and Birge 1994, Menon and Nagel 1995, Leheny *et al.* 1996), is completely due to secondary relaxation processes. In the carboranes and in 1-cyanoadamantane where such processes are absent, no excess wing is observed. Consequently, Nagel-scaling does not work for the PCs investigated. The absence of the excess wing and the failing of Nagel-scaling in this different class of disordered materials hopefully will help to clarify the origins of these intriguing properties of SGFs.

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REFERENCES

- ANDERSON, O., and ROSS, R. G., 1990, *Molec. Phys.*, **71**, 523.
- BRAND, R., LUNKENHEIMER, P., and LOIDL, A., 1997, *Phys. Rev. B*, **56**, R5713.
- BRAND, R., LUNKENHEIMER, P., SCHNEIDER, U., and LOIDL, A., 1999, *Phys. Rev. Lett.*, **82**, 1951.
- CHAMBERLIN, R. V., 1993, *Phys. Rev. B*, **48**, 15638.
- COLE, K. S., and COLE, R. H., 1941, *J. chem. Phys.*, **9**, 341.
- DAVIDSON, D. W., and COLE, R. H., 1951, *J. chem. Phys.*, **18**, 417; **19**, 1484.
- DIXON, P. K., WU, L., NAGEL, S. R., WILLIAMS, B. D., and CARINI, J. P., 1990, *Phys. Rev. Lett.*, **65**, 1108.
- GÖTZE, W., and SJÖGREN, L., 1992, *Rep. Progr. Phys.*, **55**, 241.
- HOFMANN, A., KREMER, F., FISCHER, E. W., and SCHÖNHALS, A., 1994, *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Berlin: Springer-Verlag) pp. 309–331.
- JOHARI, G. P., and GOLDSTEIN, M., 1970, *J. chem. Phys.*, **53**, 2372; Johari, G. P., 1976, *Ann. N.Y. Acad. Sci.*, **279**, 117.
- LEHENY, R. L., MENON, N., and NAGEL, S. R., 1996, *Europhys. Lett.*, **36**, 473.
- LEHENY, R. L., and NAGEL, S. R., 1997, *Europhys. Lett.*, **39**, 447.
- LESLIE-PELECKY, D. L., and BIRGE, N. O., 1994, *Phys. Rev. Lett.*, **72**, 1232; *Phys. Rev. B*, **50**, 13250.
- LUNKENHEIMER, P., PIMENOV, A., DRESSEL, M., GONCHAROV, YU. G., BÖHMER, R., and LOIDL, A., 1996a, *Phys. Rev. Lett.*, **77**, 318.
- LUNKENHEIMER, P., PIMENOV, A., SCHIENER, B., BÖHMER, R., and LOIDL, A., 1996b, *Europhys. Lett.*, **33**, 611.
- LUNKENHEIMER, P., PIMENOV, A., and LOIDL, A., 1997, *Phys. Rev. Lett.*, **78**, 2995.
- MENON, N., and NAGEL, S. R., 1995, *Phys. Rev. Lett.*, **74**, 1230.
- NGAI, K. L., 1998, *Phys. Rev. E*, **57**, 7346.
- RAMOS, M. A., VIEIRA, S., BERMEJO, F. J., DAWIDOWSKI, J., FISCHER, H. E., SCHOBER, H., GONZÁLEZ, M. A., LOONG, C. K., and PRICE, D. L., 1997, *Phys. Rev. Lett.*, **78**, 82.
- SHABLAKH, M., DISSADO, L. A., and HILL, R. M., 1983, *J. chem. Soc. Faraday Trans ii*, **79**, 369.
- SCHNEIDER, U., LUNKENHEIMER, P., BRAND, R., and A. LOIDL, 1998, *J. non-crystalline Solids*, **235–237**, 173.
- SCHNEIDER, U., LUNKENHEIMER, P., BRAND, R., and A. LOIDL, 1999, *Phys. Rev. E*, **59**, 6924.
- TARJUS, G., KIVELSON, D., and KIVELSON, S., 1997, *Supercooled Liquids: Advances and Novel Applications*, edited by J. T. Fourkas, D. Kivelson, U. Mohanty and K. A. Nelson (Washington, DC: American Chemical Society), pp. 67–81.