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## RESEARCH ARTICLE

## Pressure dependence of the dielectric loss minimum slope for ten molecular liquids

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We present a comprehensive study of data for the dielectric relaxation of ten glass-forming organic liquids at high pressure along isotherms, showing that the primary ( $\alpha$ ) high frequency relaxation is characterized well by the minimum slope and the width of the loss peak. The advantage of these two parameters is that they are model independent. For some materials with  $\beta$  processes in mHz and kHz range the high frequency slope tends to be  $-1/2$  with pressure increase. Besides the two parameters captures the relaxation shape invariance at given relaxation time but different combinations of pressure and time [6].

Glass may be regarded as the fourth state of conventional matter, isotropic as the liquid state, but solid as the crystalline state. With the notable exception of helium, any liquid may be turned into glass by cooling it fast enough to avoid crystallization [1–5].

Physical systems usually relax following perturbations forced upon them. The relaxation of the systems consists of processes going on different time scales. The dominant and slowest relaxation process of a glass-forming liquid is the so-called  $\alpha$  process. The  $\alpha$  process defines the liquid relaxation time, an important quantity because the glass transition takes place when the relaxation time significantly exceeds the inverse relative cooling rate. Compression of supercooled liquid slows down the  $\alpha$  relaxation (increases the characteristic relaxation time,  $\tau$ ). On the other hand this effect can be compensated by heating up the liquid. Different combinations of  $p$  and  $T$  can result in the same relaxation dynamics at same  $\tau$  or materials obey the temperature-pressure superposition at the same relaxation times (TTPS) [6–11]. There are different kinds of secondary ( $\beta$ ) relaxation including the Johari-Goldstein (JG) and these of intra-molecular motions [11–16] or any excess wings.

In a paper from 2001 it was shown that the high frequency slope of the dielectric loss for a group of materials tends to be  $-1/2$  as the temperature approaches the glass transition temperature,  $T \rightarrow T_g$ , and this was linked to time-temperature superposition (TTS) [17], but there is found a general prevalence of the  $-0.5$  for the slope in highly viscous liquids no matter if TTS is obeyed [18]. In those papers the dielectric scans were taken at ambient pressure. In the following is investigated: if this result holds for dielectric frequency scans for ten liquids along isotherms with increasing pressure ( $p \rightarrow p_g$ ); and if the used model-independent shape quantities, *minimum slope* and *half loss peak width* capture TTPS. The minimum slope, of course, may well be affected by secondary processes, the well expressed in the experimental frequency window as well the underlying low-frequency  $\beta$  relaxation

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1 (or an excess wing), but no attempt is made to compensate for this effects. The  
2 point is that the minimum slope is an objective shape parameter.

3 We have measured the dielectric loss,  $\varepsilon''$ , as function of frequency for a number of  
4 organic glass formers slightly below the glass transition pressure. In order to avoid  
5 bias, data were selected prior to their analysis. A model-independent data analysis  
6 was performed, i.e., without fitting data to any of the standard functions (stretched  
7 exponential, Havriliak-Negami, Cole-Cole, Cole-Davidson, etc.). Thus there is no  
8 need distinguish between liquids with and without clearly resolved secondary ( $\beta$ )  
9 processes. Very accurate data are required in order to obtain reliable slopes by  
10 numerical differentiation. The selection criteria were low noise, well defined loss  
11 peak, and sufficient length of the high frequency part of the dissipation in order  
12 to find the minimum slope. In order to avoid bias, data were selected prior the  
13 analysis. The data analysis was automated as far as possible via Matlab programs  
14 used in [18].

15 Moreover, following the philosophy of making as direct and unbiased data anal-  
16 ysis as possible, no attempt was made to subtract possible contributions from DC  
17 conductivity. Of course if the conductivity overrules the primary relaxation then  
18 the particular scan was excluded from the analysis. In order to avoid the influence  
19 of the conductivity was a frequency scan discarded if one of the following points  
20 was not fulfilled: the low frequency slope is one (within the measure noise); or TTS  
21 around the loss peak is obeyed (of course in a range where  $\beta$  relaxation does not  
22 interfere) [19].

23 The chemicals are chlorinated biphenyl (CBP, Aroclor [16]), 1,1'-bis (p-  
24 methoxyphenyl) cyclohexane (BMMPC [20]), Di-*iso*-butyl phthalate (*Diso*BP,  
25 [21]), di-propylene glycol (DPG, [22]), tri-propylene glycol (TPG, [10]), digly-  
26 cidyl ether of bisphenol-A (EPON828, [23]), propylene carbonate (PC,[8]),  
27 phenolphthalein-dimethylether (PDE [24]), tetramethyltetra-phenyltrisiloxane  
28 (DC704, this work, Dow Corning 704® diffusion pump fluid), perhydroisoquino-  
29 line (decahydroisoquinoline, PHIQ, this work, 99% , Aldrich, Fig. 1(b)). DC704  
30 is represented on Figure 1(a) with three isotherms  $T = 253\text{K}$   $p \in [6; 2460]$  bar,  
31  $T = 263\text{K}$   $p \in [1333; 2404]$  bar and  $T = 283\text{K}$   $p \in [2559; 2404]$  bar, and PHIQ  
32 with two isotherms on Figure 1(b)  $T = 232\text{K}$   $p \in [0; 1000]$  bar and  $T = 293\text{K}$   
33  $p \in [3375; 17500]$  bar. The measurements were carried out on the set up described  
34 in [25, 26]. The pressure-transmitting liquid was a silicon oil. The measure cell  
35 consist of a capacitor - two parallel parts of the steel cylinder, separated by Teflon  
36 stripes and kept together by two Teflon rings - placed into a tightly closed Teflon  
37 container filled up with the sample liquid [27].

38 The low-frequency (long-time) properties of the  $\alpha$  process are fairly trivial; the  
39 vast majority of glass-forming liquids here exhibit what corresponds to a cut-off  
40 in the relaxation time distribution function at long times [26, 28, 29]. Focusing  
41 on the short-time (high-frequency) relaxation properties, at each temperature and  
42 pressure we identified the minimum slope in the standard log-log plot,  $\alpha_{min} \equiv$   
43  $\min(d \log \varepsilon'' / d \log f) < 0$ , where  $f$  is frequency and  $\log$  is the base-10 logarithm  
44 (see Fig. 2(a)). This identifies the inflection point above the loss-peak frequency.  
45 The number  $\alpha_{min}$  gives the best approximate inverse power-law description of the  
46 loss decay above the peak:  $\varepsilon''(f) \propto f^{-|\alpha_{min}|}$  applies to a good approximation over a  
47 significant frequency range. Only data with a well-defined minimum slope or a clear  
48 slope plateau in the point-by-point numerical differentiation were used. If there  
49 appears relatively low noise in the derivative a smoothing is obtained by averaging  
50 the values (Fig. 2(a)) and the minimum value found. The averaging was done to  
51 maximize the number of data sets. The distribution of the minimum slopes for the  
52 ten different liquids for all temperatures and frequency-pressure scans is presented  
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60

1 at Figure 2(b). The above-mentioned limitations as well as the different pressure  
2 and frequency ranges and intervals imply that the number of data sets (isotherms)  
3 per liquid varies from 1 to 3, as well the number of data points (pressures) for each  
4 dataset at constant temperature for a liquid varies from 4 up to 26. To compensate  
5 for this we give equal weight to each liquid in Figure 1(b). If  $N$  is the number of  
6 data points were included in the analysis for a given liquid at one temperature and  
7  $n$  is the number of isotherms for this particular liquid, each each minimum-slope  
8 observation was weighted by a factor  $1/(Nn)$  for this isotherm.  
9

10 We find slightly different result as we had previously observed for liquid dynamics  
11 controlled by temperature changes [18]. The histogram on Fig. 2(a) shows that the  
12 high frequency relaxation of viscous liquids squeezed at constant temperature is  
13 most often characterized with  $-0.45 < \alpha_{min} < -0.35$ . In the previous study of  
14 dielectric response of 52 liquids at ambient pressure most represented value interval  
15 for minimum slope is around  $-0.5$  or more precisely, approximately 45% of the  
16 observed values of minimum slope are  $-0.55 < \alpha_{min} < -0.45$  [18]. The number of  
17 different chemicals is too small to conclude anything about the generality of this  
18 observation. Therefore we have to look more detailed how  $\alpha_{min}$  does change with  
19 compression in order to find what are the tendencies.  
20

21 Figure 3(a) shows a minimum-slope evolution with loss peak frequency. It can  
22 be seen that it is similar to temperature data at ambient pressure [17, 18, 33], the  
23 high frequency slope of the dielectric dissipation may converge slowly to  $-1/2$  as  
24 pressure increases.  
25

26 In attempt to describe the shape of the  $\alpha$  relaxation fully we need second shape  
27 parameter. We use the quantity width,  $W$ , at half dissipation maximum in decades.  
28 In an attempt to use as many data sets as possible and to avoid the effect of DC-  
29 contribution to the left of loss peak we use only the number of decades of frequency  
30 on the right the loss peak,  $W_{\frac{1}{2}}$ . From observations of different master curves the  
31 following can be stated more or less generally that - if there are changes in the shape  
32 of the loss, these are mainly due to changes of the slope of the high frequency part.  
33 Thus we can expect the same information about the shape from the full width and  
34 as well from the width between the frequency at loss peak and the highest frequency  
35 corresponding to half loss. Here we normalized the width  $w_{\frac{1}{2}}$  with respect to the  
36 half Debye width  $W_D/2 \approx 0.572$ . If  $w_{\frac{1}{2}} = \frac{W_{\frac{1}{2}}}{W_D/2} \rightarrow 1$ , then the relaxation is Debye-  
37 like. The plot of the  $w_{\frac{1}{2}}$  as function of the frequency is on Figure 3(b). The width  
38 follows qualitatively the behavior of  $\alpha_{min}$  to some extension, but seems that it is  
39 less sensitive to temperature or pressure changes than the minimum slope.  
40  
41

42 Figure 3 is in agreement with findings regarding temperature pressure super-  
43 position at same relaxation times that the dielectric relaxation for some liquids  
44 the depends only on the relaxation times and not the temperature or pressure [6].  
45  $\alpha_{min}$  together with  $w_{\frac{1}{2}}$  as functions of the frequency describe the changes in the  
46 shape of high frequency dielectric loss at some relaxation time. If minimum slope  
47 and width for two or more isotherms lays on the top of each other, means that  
48 the relaxation has the same shape for  $f > f_{max}$  to the inflection point. Thus from  
49 this plot can also be estimated the frequency below which the  $\alpha$  relaxation (high  
50 frequency part) is no longer affected by secondary processes that appears at times  
51 that are smaller than the  $\alpha$ -relaxation time and do not couple to pressure and tem-  
52 perature in the same way as the primary process. This happens at frequency where  
53 the shape quantities' curves join into one, i.e., the relaxation time determinate the  
54 shape of the relaxation and that is coinvariant of temperature or pressure changes  
55 [6].  
56  
57

58 The pressure-temperature superposition at the same relaxation time is relatively  
59  
60

well obeyed in the case of the van der Waals liquids PC (dark green), PDE (brawn), and DC704 (black) if we look on both shape parameters  $\alpha_{min}$  and  $w_{\frac{1}{2}}$ . In contrast to the plot of TPG data (orange) it can be seen that the primary process shape is dominated by the secondary relaxation at pressures less than this that is corresponding to loss peaks above 10 Hz. In case of PHIQ (light green) one can even see on Figure 3(a) that a TTPS is not observed in the measured frequency window. The same phenomena is observed for PHIQ at ambient pressure [32] as well under pressure [31] where are even indefied two types secondary relaxations. The dielectric relaxation for this liquid is characterized by a  $\beta$  process with relatively high amplitude. The other liquids with secondary processes above 1kHz we can see that deviations in to  $\alpha_{min}$  isotherms are relatively small and the  $\beta$  process is characterised by low amplitude compared to the loss peak. It is clear that the temperature governs the  $\beta$  process amplitude as well the influence on  $\alpha_{min}$  value: higher temperature is, larger  $\alpha_{min}$  at the same relaxation time is. From this we can state that TTPS (and TTS) can only be observed if the influence of the  $\beta$  process is relatively small. The spectra for DC704 shows a secondary process with relatively low amplitude around 1MHz. Thus the  $\alpha$  relaxation observed near  $p_g$  is well separated from  $\beta$ , and therefore  $\alpha_{min} = 0.048$  is nearly constant over 4 frequency decades.

What about the liquids like PC and PDE? They have minimum slopes numerical bigger than 1/2 and they are reported to have presence of a hidden JG  $\beta$  relaxation that is coupled to the  $\alpha$  process and therefore the excess wing in relaxation are invariant to pressure and temperature, when compared at a fixed value of the  $\alpha$ -relaxation time [8, 16].

Regarding the values of  $\alpha_{min}$  one might intuitively expect that interference from  $\beta$  processes can only explain minimum slopes that are numerically smaller than 1/2. Although for many years it was believed that secondary processes are found only in the kHz-MHz frequency range, it is now generally recognized that these processes in some cases take place at much lower frequencies [30, 34]. From measurements on liquids with a well-defined  $\beta$  process in the kHz range, however, we and others (see fx. in [35]) consistently find that when the liquid is cooled down to a temperature *above* the temperature where  $\alpha$  and  $\beta$  processes merge, the high-frequency decay of the “collapsed” alpha-beta process has a minimum slope that is usually numerically larger than 1/2. The same should be expected for pressure sensitive time scale of  $\beta$  process. Thus, since whenever there are low-lying  $\beta$  processes the liquid is unavoidably around or above the  $\alpha$ - $\beta$  merging temperature or under the merging pressure,  $|\alpha_{min}| > 1/2$  might occur as in case of PC [8] or PDE [24]. This means that in this liquids might not happen a separation of the processes and thus TTPS is obeyed. PDE’s relaxation under  $T_g$  at ambient pressure shows two secondary processes [36]. If the dissipation is characterized with a well defined  $\beta$  process then  $\alpha_{min} \rightarrow -\frac{1}{2}$ . In other words, “genuine”  $\alpha_{min} = -1/2$  behavior only appears when the system is significantly below the merging temperature or above the merging pressure as in the case of DC704.

An obvious question is whether the observed prevalence of minimum slopes around  $-0.4$  is general or we should expect a value of  $-0.5$ . If  $\alpha_{min} = -1/2$  was significant, one would expect that the closer the minimum slope is to  $-1/2$ , the better an inverse power-law description applies. This is investigated in Figure 4(a) that plots the third-order derivative relative to the first-order derivative,  $|H^{(3)}(x_0)/\alpha_{min}|$ , where  $H(x) = \log \varepsilon''(x)$ ,  $x = \log f$ , and  $x_0$  is the log frequency at the point of minimum slope. The idea is that, since the second-order derivative is zero at the frequency of minimum slope, by Taylor’s formula the smaller  $|H^{(3)}(x_0)/\alpha_{min}|$ , the larger the frequency range is, where the slope is almost con-

1 stant. Figure 4(a) shows that the better an inverse power law describes the loss,  
2 the closer  $\alpha_{min}$  is to  $-1/2$  for DisBP (red +) and EPON828 (cyan). For DC704  
3  $|H^{(3)}(x_0)/\alpha_{min}|$  lowers with pressure while  $\alpha_{min}$  values are nearly constant that  
4 means - the  $f^{|\alpha_{min}|}$  applies to bigger frequency range. The increase and afterwards  
5 decrease in  $|H^{(3)}(x_0)/\alpha_{min}|$  values (with in the noise) captures the  $\alpha - \beta$  merging  
6 process in the relaxation of BMMPC (blue) around 1Hz and DPG (magenta) at  
7 100Hz (but DPG has more complex relaxation due to two  $\beta$  processes[37, 38]).

8 Let us again see on the information that we can extract from Figure 4(a) about  
9 the excess wing relaxations. For PDE the value of  $|H^{(3)}(x_0)/\alpha_{min}|$  decreases with  
10 pressure increase but it begins to increase slowly again. So from a certain relax-  
11 ation time (pressure) the frequency range of  $-\alpha_{min}$  slope approximation begins  
12 to be smaller. This is indication of  $\alpha - \beta$  merging process between 1 and 0.1 Hz.  
13 This might be the case for CBP (yellow) as well. We can not say anything consist-  
14 ent about PC relaxation pattern. The experiential that window is rather narrow.  
15 Confirmation of this observation for this liquids should be done on dielectric mea-  
16 surements at higher pressures.

17 The linearity of the minimum-slope pressure dependence can be seen on Figure  
18 4(b) plotting the change in slope point-by-point of the  $\alpha_{min}$  curves with the slowing  
19 of the relaxation. For DC704 that has a numerical minimum slope of 0.48,  $\alpha_{min}$   
20 is constant. While for all other liquids  $\alpha_{min}$  is changing in such way that if  $\alpha_{min}$   
21 approaches  $-0.5$ , then its value is rather constant. It is interesting that materials  
22 with values of  $\alpha_{min}$  numerically bigger than  $1/2$  like for PC have minimum slope  
23 that changes very "slowly" and almost linearly with  $\log f$  over more than 6 decades.  
24 Thus one can expect that generally  $\alpha_{min}$  will change until it reach 0.5 and will be  
25 constant. One apparent exception is PDE. It seems to have a constant  $\alpha_{min}$  around  
26  $-0.6$  (Fig. 4(b) and 3(a)), but together with the Figure 4(a), can be a sign of a  
27 hidden  $\beta$  process at frequencies under 1Hz that can contribute to the primary  
28 process as in the case of DPG.

29 In conclusion, the minimum slope and the width of the loss peak - shape pa-  
30 rameters that describes only the high frequency part of the dispersion - capture  
31 excellently the superposition of loss with same relaxation times but at different  
32 temperatures and pressures. The considerable advantage of these two parameters  
33 is that they are model-free and thus independent of fitting procedures. With com-  
34 pression of the viscous liquid the minimum slope value may converge to  $-1/2$  (Fig.  
35 2(a)) as the  $\alpha$  and  $\beta$  processes separate (Fig. 4(a)). The deviations from this power  
36 law are most likely due to interference from one or more secondary relaxation pro-  
37 cesses, with or without distinct maxima. If one or more secondary processes appear  
38 in the Hz range, it is practically impossible to separate  $\alpha$  and beta processes and  
39 this will be mirrored in the value of the minimum slope.

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35 of the sample from the pressure transmitting liquid – silicon oil. The observed DC conductivity results  
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1  
2  
3 Figure 1. Full data set log-log plot of the dielectric loss  $\varepsilon''$  as a function of frequency for (a): DC 704  
4 at  $T = 253\text{K}$   $p \in [6; 2460]$  bar (black - -),  $T = 263\text{K}$   $p \in [1333; 2404]$  bar (red -) and  $T = 283\text{K}$   
5  $p \in [2559; 2404]$  bar (blue - · -). There is a secondary process at 0.1 – 1MHz that is relatively pressure  
6 insensitive. (b): PHIQ at  $T = 232\text{K}$   $p \in [0; 1000]$  bar (black - · -) and  $T = 293\text{K}$   $p \in [3375; 17500]$  bar  
7 (red +). The scan is characterized by a well resolved pressure-independent  $\beta$  process with relatively high  
8 amplitude at 1MHz. Only few of the presented are used in the analysis.

9  
10 Figure 2. (a): The slope of the double logarithmic dielectric dissipation (with stars) at some chosen  
11 pressures from the data on Figure 1(a) DC704 at 253K. The green line indicates the averaged values that  
12 are used to find the minimum slope,  $\alpha_{min}$ .  
13 (b): Histogram of the minimum-slope distribution for the ten organic glass-forming liquids (one column for  
14  $-0.85 < \alpha_{min} < -0.75$ , one for  $-0.75 < \alpha_{min} < -0.65$ , etc). Since the number of pressures investigated  
15 varies from isotherm to isotherm as well the number of isotherms for each liquid, each minimum slope  
16 observation is weighted by a factor  $1/(Nn)$ .  $N$  is the number of data points (pressures) in a data set for  
17 the given liquid at the given temperature, and  $n$  is the number of isotherm data sets for the given liquid.  
18 In this way all liquids contribute equally to the histogram. Note that a isotherm may contribute to more  
19 than one column in this figure since  $\alpha_{min}$  vary with pressure.

20 Figure 3. (a): The minimum slope  $\alpha_{min}$  plotted as a function of pressure quantified by the position of  
21 the loss peak frequency  $f_{max}$  for all 9 liquids along isotherms. Every liquid has its own color.  
22 (b): The evolution of the half width at half maximum in decades write for the loss peak and normalized  
23 with the same quantity for a Debye process defined as  $w_{\frac{1}{2}} = \frac{W_{\frac{1}{2}}}{W_D/2}$ , where  $W_{\frac{1}{2}}$ , is the number of decades  
24 of frequency on the right of the loss peak normalized with respect to the half Debye width  $W_D/2 \approx 0.572$   
25 ( $w_{\frac{1}{2}} \rightarrow 1$  indicates Debye-like relaxation). In this plot the data points for PHIQ are absent because the  
26 corresponding loss at the frequency at half maximum loss coincides with the  $\beta$  relaxation loss.

27 Figure 4. (a): Third-order relative to first-order derivative,  $|H^{(3)}(x)/\alpha_{min}|$ , at the frequency of minimum  
28 slope for all data sets where  $H(x) \equiv \log \varepsilon''(x)$  ( $x = \log f$ ). At the frequency of minimum slope the second-  
29 order derivative is zero; thus by Taylor's formula the smaller the third-order derivative is relative to the  
30 first-order derivative  $\alpha_{min} = H'(x)$ , the better an inverse power law description of the high-frequency loss  
31 applies.  
32 (b): The slope of  $\alpha_{min}$  is giving information how much  $\alpha_{min}$  is pressure dependent. Both quantities  
33 contain information about the time scales of the secondary processes.

Fig.1

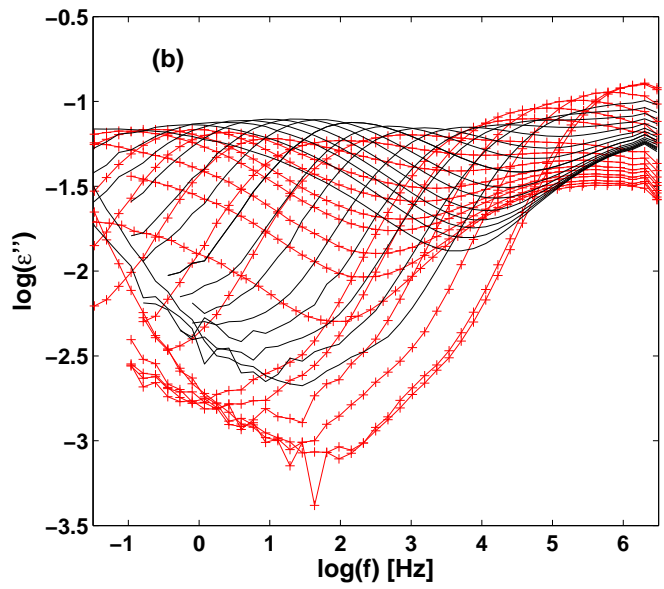
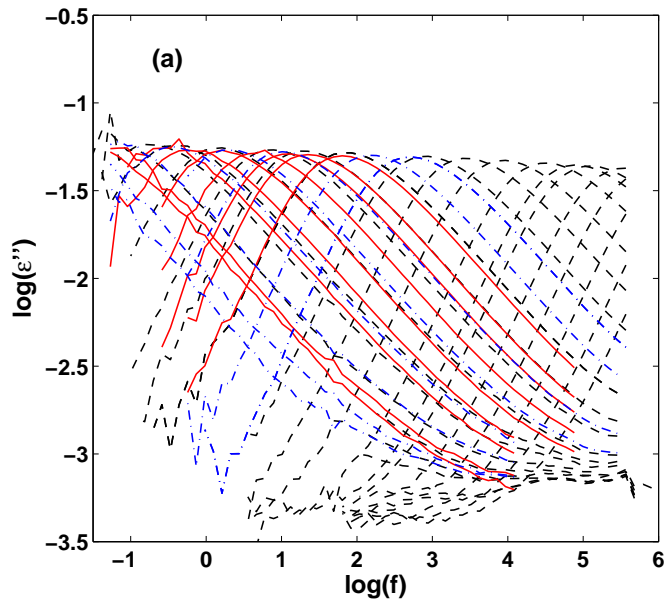


Fig 2

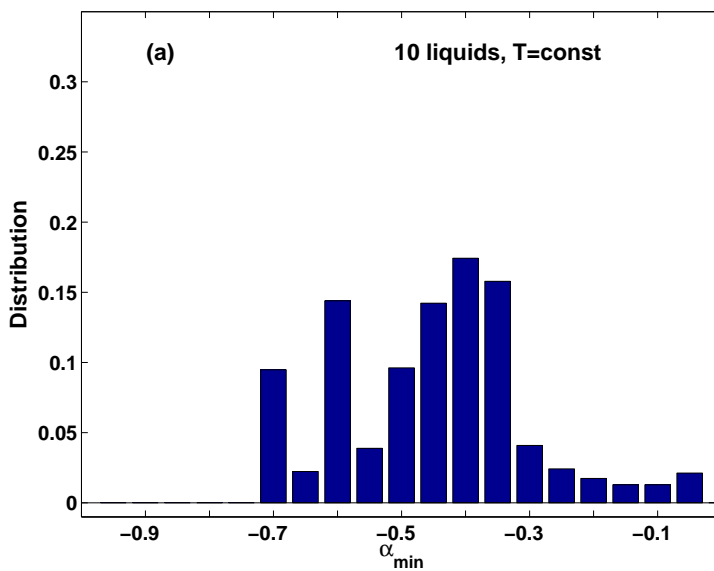
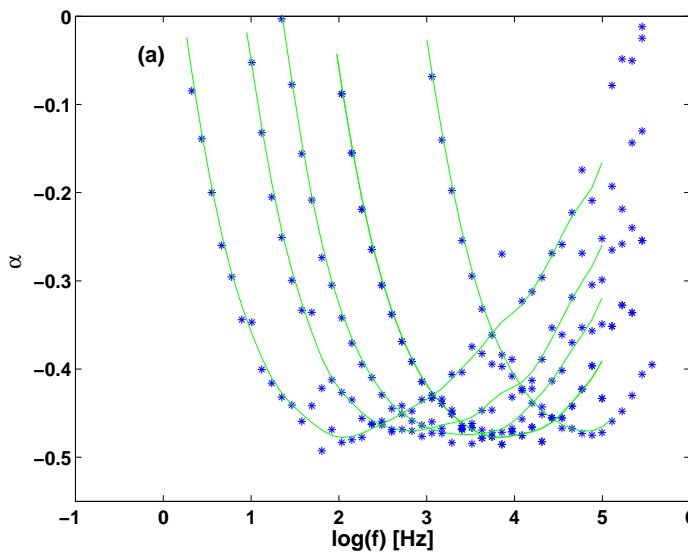


FIG 3.

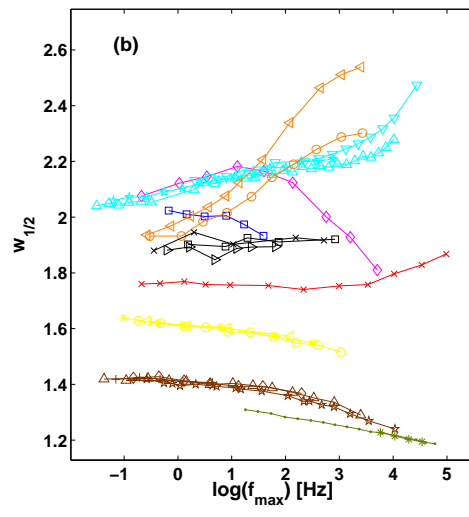
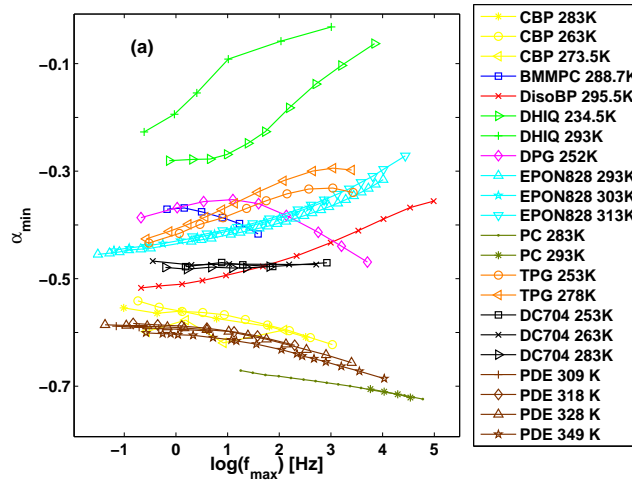
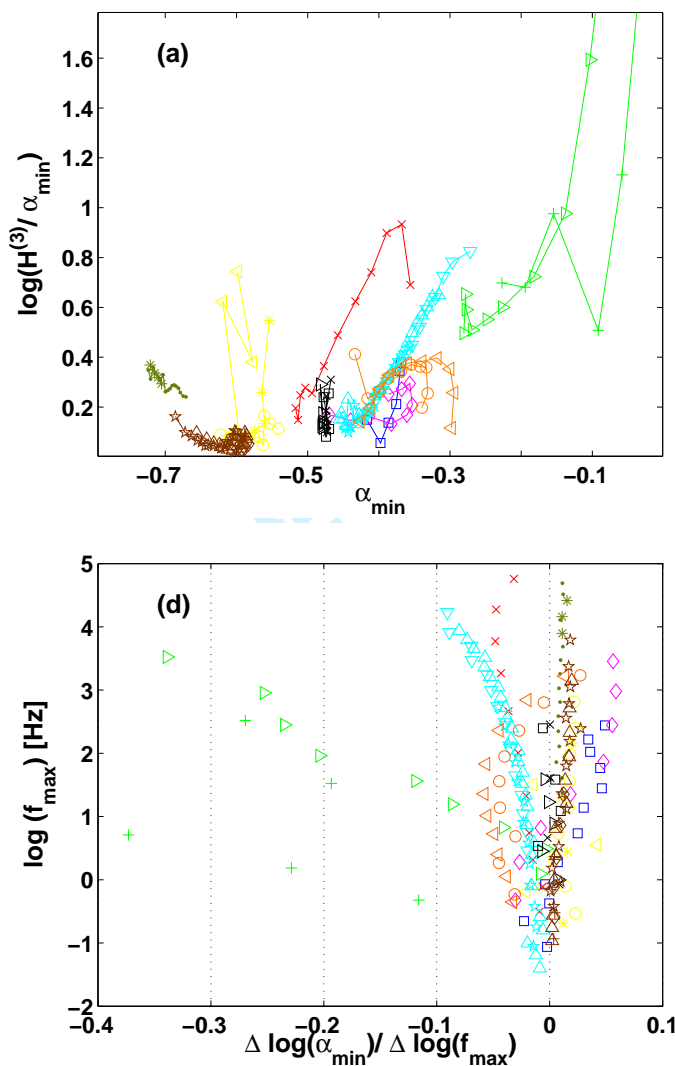


FIG 4.



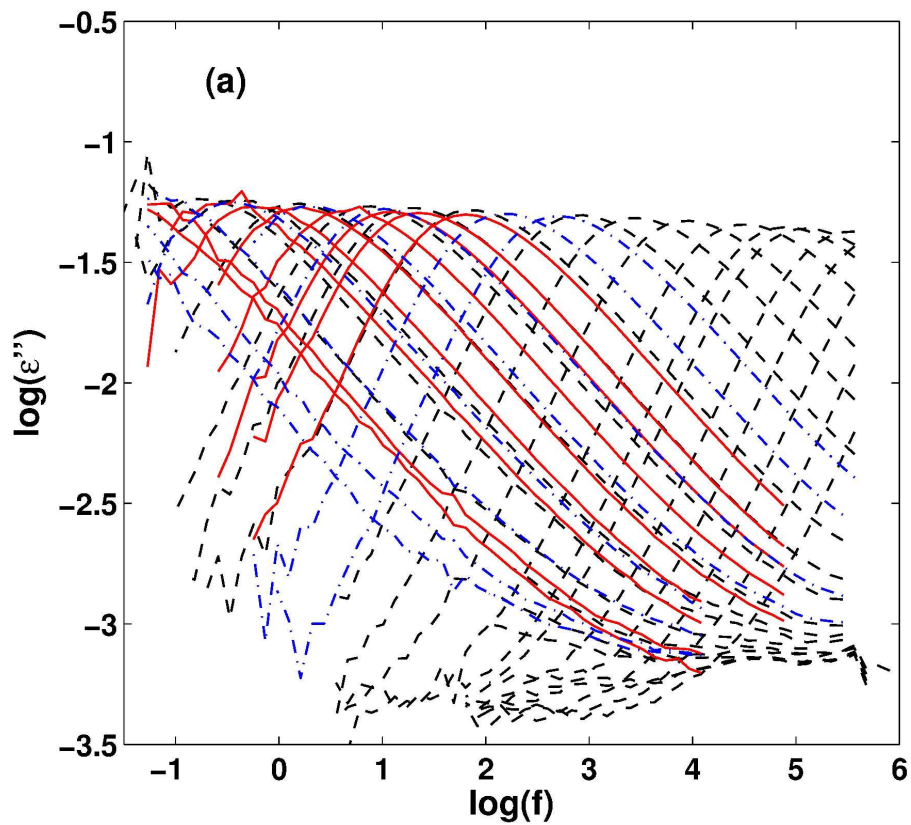


Figure 1  
164x145mm (600 x 600 DPI)

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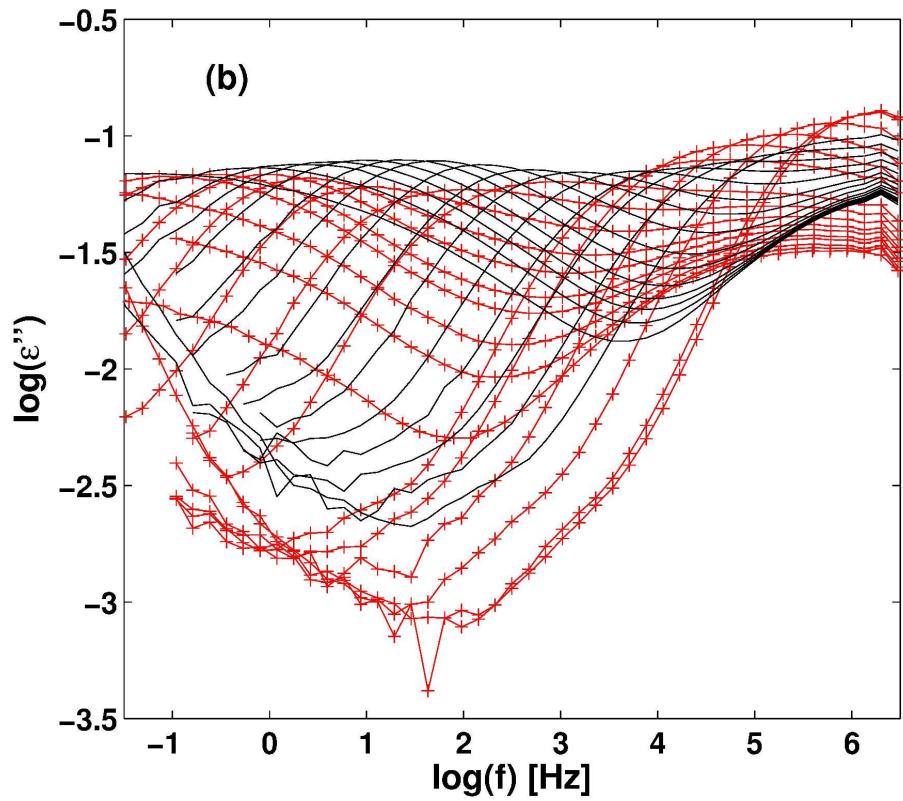


Figure 1  
164x140mm (600 x 600 DPI)

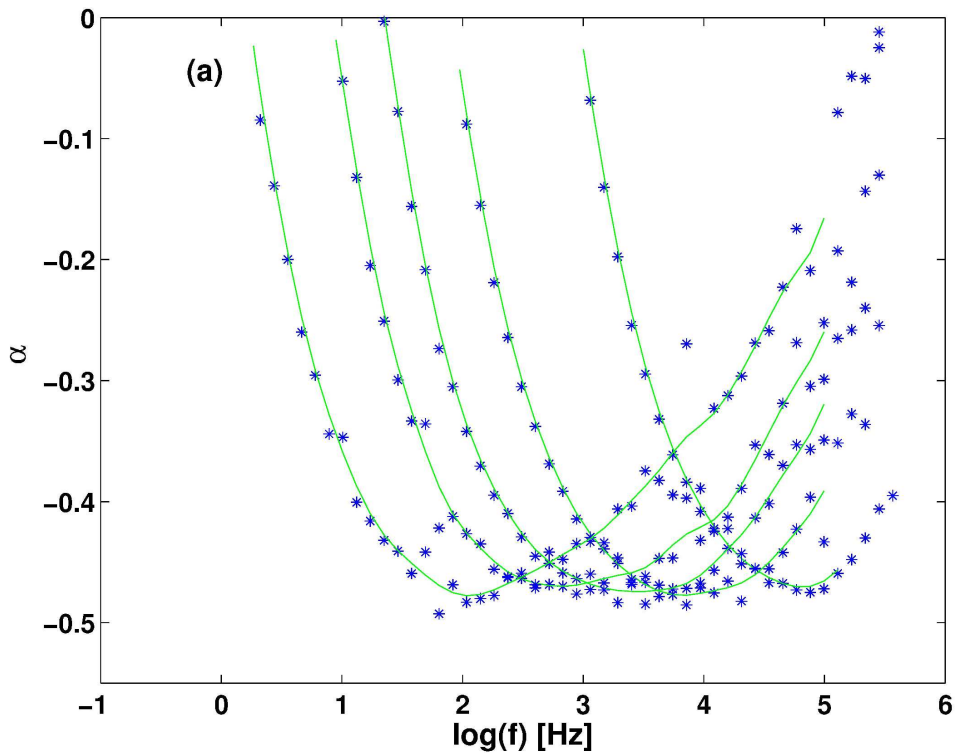


Figure 2  
186x150mm (600 x 600 DPI)

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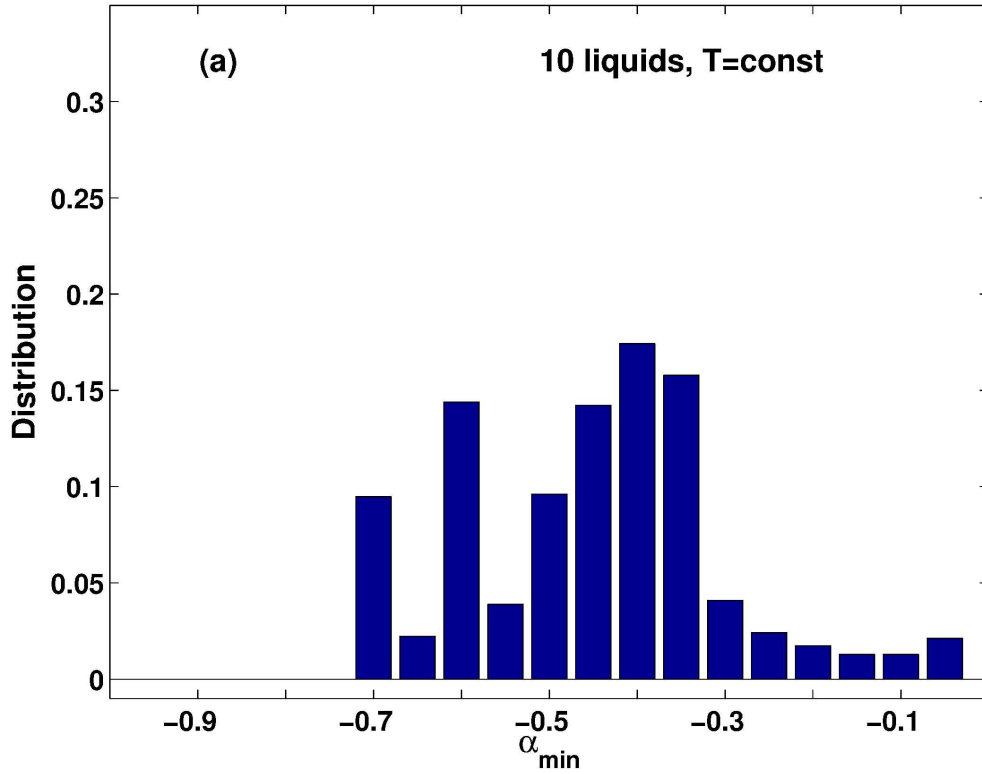
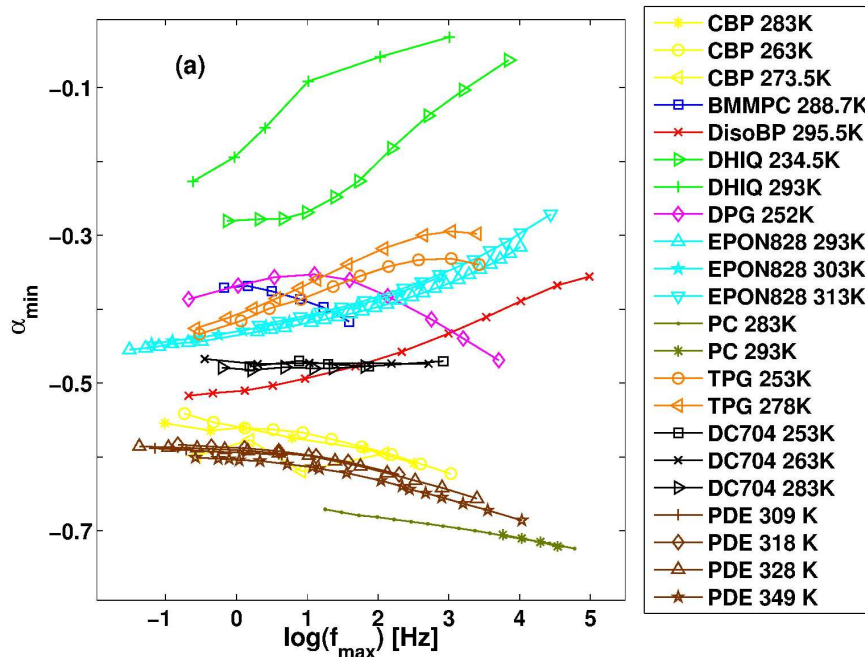


Figure 2  
179x142mm (600 x 600 DPI)

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222x158mm (600 x 600 DPI)

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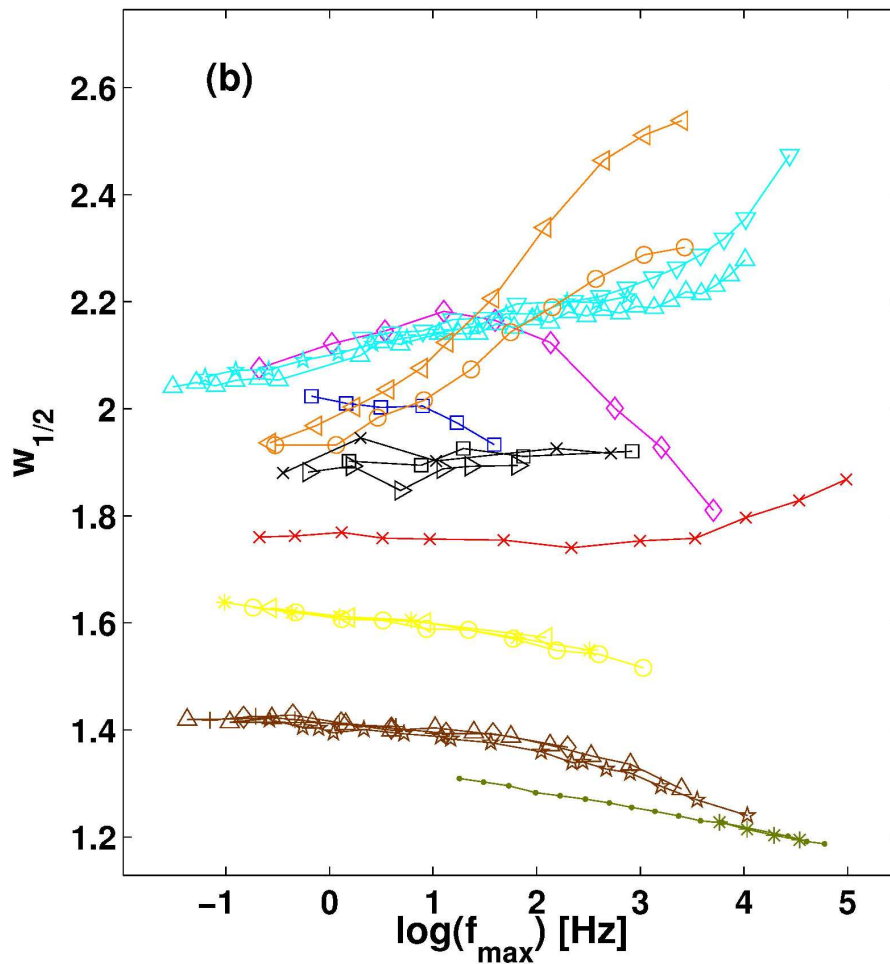


Figure 3  
149x158mm (600 x 600 DPI)



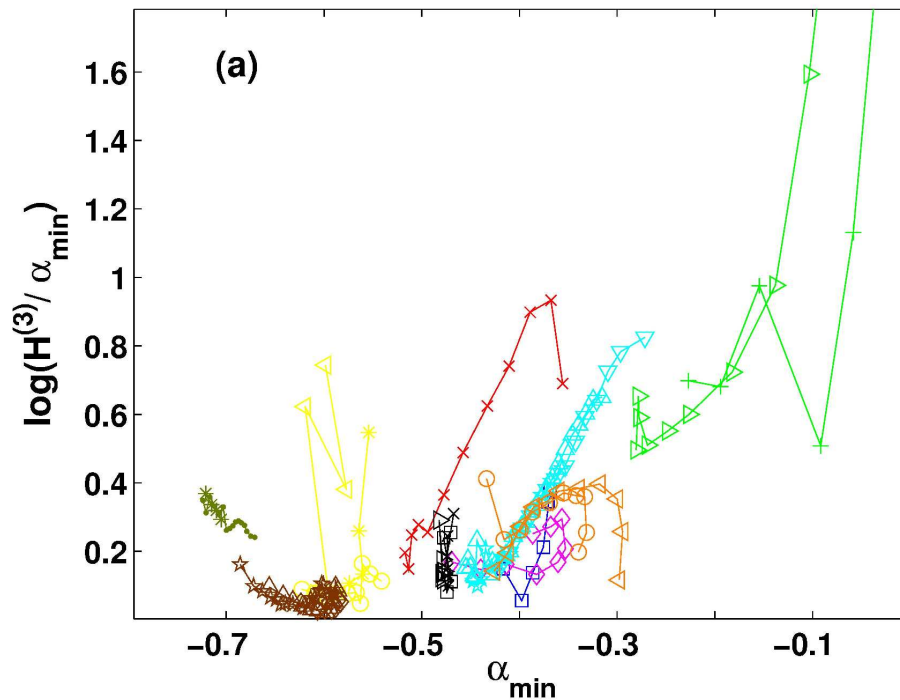


Figure 4  
158x118mm (600 x 600 DPI)

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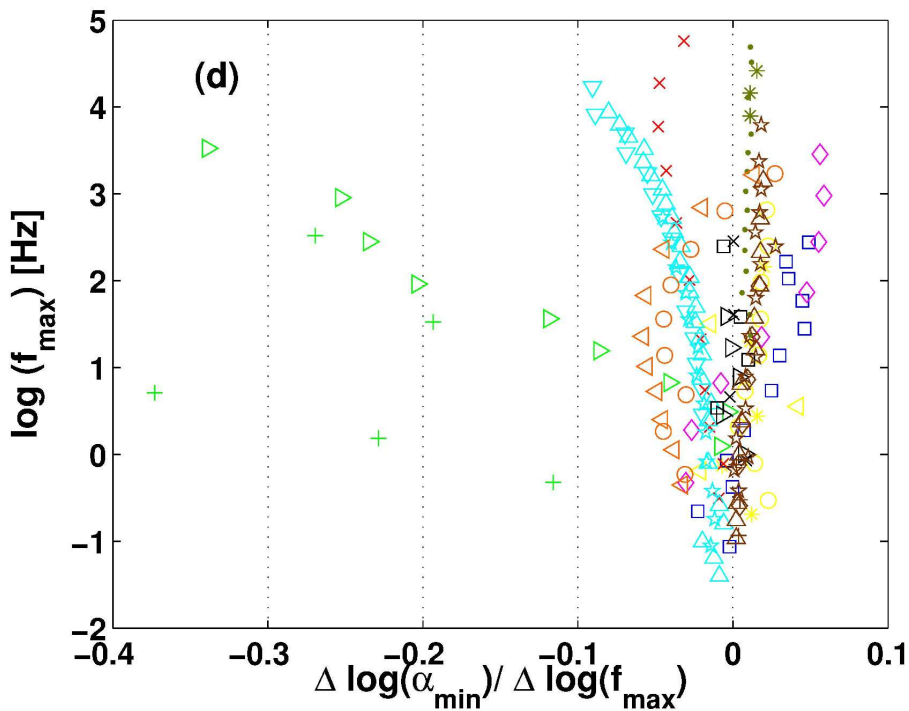


Figure 4  
158x118mm (600 x 600 DPI)

Pre-proof Only