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Effect of pressure on relaxation dynamics at different time scales in supercooled systems

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Abstract

Dynamics of two glass-forming systems have been investigated by means of dielectric spectroscopy over 10 decades under cooling (from melting point to well below the glass transition temperature) and under compression (from atmospheric pressure up to 700 MPa). The α -relaxation time τ_α resulted to be significantly affected by both thermodynamic variables, showing their equivalent role in slowing down the dynamics. Some deep similarities were found: for instance, the dispersion of the α -process was shown to increase with decreasing temperature T and increasing pressure P . Furthermore, the same shape for relaxation dynamics over a broad time-scale was found by comparing two dielectric loss spectra obtained at different T and P but characterized by the same $\tau_\alpha(T,P)$. Additionally, it is noteworthy that the effect of T and P on slowing down the time scale of fast relaxation processes (β -relaxation and excess wing), although less strong than in the case of α -process, was again comparable. These evidences demonstrate that in the investigated systems: a) slow and fast relaxations are strongly related; b) the shape of α -relaxation and c) the separation between α - and β -relaxation time scale are controlled by $\tau_\alpha(T,P)$ and not by separate thermodynamic variables.

Keywords: glass transition; pressure; dispersion; dynamic heterogeneity; structural relaxation; β -relaxation

AMS Subject Classification:

Introduction

On decreasing temperature T or increasing pressure P a glass-forming liquid will vitrify; that is, the structural relaxation time, τ_α , becomes so long that eventually the system cannot attain an equilibrium configuration in the available time. The importance of glass transition for science and technology drove research efforts over the last decades with the task of understanding the underlying mechanism of relaxation and finding out the ruling factors for the slowing down of the dynamics [1]. These factors have been identified and incorporated into recent theories and models of the glass transition. The factor governing the divergence of τ_α with decreasing T at constant P was identified, for instance, as unoccupied volume in the free volume model [2], and configurational entropy in the Adam and Gibbs [3] model. An increase of P (i.e. a decrease of specific volume v) at constant T reduces both the unoccupied volume and the configurational entropy, thus slowing down the structural relaxation. The free volume model has been extended to consider the effect of hydrostatic pressure [4], and an extension of the Adam-Gibbs model for

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elevated pressures has been proposed as well [5]. Recently, it has been shown [6, 7, 8] that the behaviour of relaxation times $\tau_\alpha(T, \nu)$ for different T and ν collapses to a master curve when plotted versus $T\nu^\gamma$, with γ a material constant related to the steepness of the intermolecular repulsive potential [6] or to thermodynamic properties of the system [9]. In spite of differences in the physics underlying the various theories of the glass transition, a common feature of all these models is that the dispersion (time or frequency dependence) of the structural relaxation bears no relation to the structural relaxation time and no constraints to the dynamic properties or for the variation of dispersion are provided. Usually, dispersion is not considered at all or, at best, it is derived as a separate consequence of the model based on other factors possibly entailing additional assumptions. Consequently, the dispersion and τ_α are obtained independently as separate and unrelated predictions and it is likely that, even if τ_α can be constant for different combinations of T and P because of compensating effects on the molecular mobility, the dispersion is not expected to scale in the same way. Such approaches appear to be incompatible with a general experimental fact recently discovered in glass-formers [10]: for a given material at a fixed value of τ_α , the dispersion is constant, independent of thermodynamic conditions (T and P); that is, even if it is changing with T or P , the shape of the relaxation function depends only on the relaxation time. For instance, if the structural relaxation function is represented by a Kohlrausch-Williams-Watts (KWW) function, then the stretching parameter β_{KWW} is a direct function only of τ_α , i.e. $\beta_{KWW}(\tau_\alpha)$. If the dispersion of the structural relaxation was derived independently of τ_α , the relation $\beta_{KWW}(\tau_\alpha)$ would be an unlikely result. Moreover, if the effect of T and P on structural dynamics has been extensively studied, few studies [12, 14] were devoted in investigating the behavior of secondary relaxations, especially those usually referred as Johari-Goldstein (JG) process, a small angle motion of the entire molecule as a whole [13, 15], an universal process typical of glassy state, closely related to the α -process. According to Coupling Model the JG process is identified with the primitive relaxation, the precursor of the α -relaxation [13, 14]: due to many-molecules dynamics, its time scale $\tau_p = \tau_{JG}$ and τ_α are related by the following relation:

$$\tau_\alpha = (\tau_{JG} t_c^{-n})^{1/n} \quad (1)$$

where $t_c = 2$ ps and n is the coupling parameter, which is related to the stretching of the Kohlrausch Williams Watts (KWW) function reproducing the structural peak, $n = 1 - \beta_{KWW}$, and it is usually considered a measure of the intermolecular coupling. For larger values of n , the intermolecular coupling is higher, and the separation of the JG peak from the structural one, i.e. τ_α / τ_{JG} , is larger. According to this model, a close relation is expected between time scales of slow (τ_α) and fast (τ_{JG}) relaxation and the dispersion of structural dynamics (β_{KWW}), and this relation is expected to hold also at different T and P . In fact, from eq.(1), one can deduce that, at constant τ_α , since the stretching parameter β_{KWW} (and so n) is constant [10], then τ_{JG} is also constant, independent of the value of T and P .

In this paper we present representative experimental results for two glass-formers, between them only one showing a well resolved JG relaxation. P and T affect dynamics at different extent over different time scales, more effective on slow (α -) than on fast (JG) relaxation. The dispersion of the structural relaxation varies over the investigated range, but it remains unchanged for largely different combinations of T and P , once τ_α is fixed. Therefore, this evidence implies that the dispersion of the structural relaxation is defined by τ_α . Also the time scale separation between structural and JG peak is defined by τ_α and dispersion itself.

Experiment

Diphenyl-vinylene carbonate (DPVC) was obtained from Aldrich. Its molecular weight is 348.15 g/mol and its T_g is 251 K. Benzoin-isobutylether (BIBE), obtained from Aldrich, was purified by distillation following the procedure illustrated in ref.[11]. Its molecular weight is 268 g/mol and its T_g is 220 K. Dielectric measurements, both at atmospheric and at high pressure were carried out

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using a Novocontrol Alpha-Analyzer ($\nu=10^2\text{-}10^7$ Hz). For atmospheric pressure measurements, a parallel plate capacitor separated by a quartz spacer (geometric capacitance ~ 90 pF) and filled by the sample was placed in the nitrogen flow Quatro cryostat. For high pressure measurements, a sample-holder multi-layer capacitor (geometric capacitance ~ 30 pF) was isolated from the pressurizing fluid (silicon oil) by a Teflon membrane. The dielectric cell was then placed in a Cu-Be alloy high pressure chamber, provided by UNIPRESS, connected to a manually operated pump with a pressure intensifier. Temperature was varied in the interval 235–310 K and controlled within 0.1 K by means of a thermally conditioned liquid flow.

Results and Discussion

Loss spectra of DPVC are shown in Fig.1 for different combinations of T and P. Looking to one spectrum and spanning the frequency interval, three region can be found: a) at low frequency a d.c. conductivity (due to drift of ionic impurities) dominates with a contribution reciprocal of frequency; b) then the peak related to the α -process, that can be well represented by the Fourier transform of the KWW function (see figure); c) at higher frequencies, no evidence of any additional (secondary) peak can be found, but only an extra loss contribution (called excess wing, EW) to the high frequency side of the α -peak, that can be represented as a power law with a smaller slope than that characterizing the high frequency side of the structural peak (see dashed lines in Fig.1). The microscopic origin of the EW has been widely debated. Some approaches, basing on scaling arguments, proposed that EW is an inherent part of the α -relaxation [16, 17]. Actually, some experimental results cast doubts on the validity of this explanation and suggested, on the contrary, that EW is nothing but the high frequency side of a JG peak submerged by the structural one and closely connected to it. For instance, EW was observed to transform into a resolved JG peak after aging at T below T_g [18, 19] or at high pressure [20], and for dielectric spectra of binary mixtures composed by mixing a polar glass former, showing EW, with one having negligible dielectric signal, the EW evolves into a secondary peak on decreasing polar component concentration [21, 22]. Therefore, the spectra in Fig.1 were fitted with a superposition of the d.c. conductivity contribution ($\sigma_{dc}/\omega\epsilon_0$), the one-side Fourier Transform of the KWW function for the structural peak and a Cole-Cole (CC) function $\Delta\epsilon/[1+(j\omega\tau)^\gamma]$ for the EW, where γ is the high frequency slope of the spectrum. We have to point out that the choice of a CC function to fit the EW contribution, although already previously adopted in literature [18], is somehow arbitrary: in fact, as long as the loss peak maximum is not visible, the relaxation time τ cannot be assessed in an unique way, without any assumption on dielectric strength $\Delta\epsilon$. Here, we are mainly interested to use this procedure just to describe the spectra and to determine the parameter γ , that is the high frequency slope. Decreasing T at fixed P or increasing P at fixed T causes a shift of the loss peak to lower frequencies. The shape of the α -process as well as of EW and that of the overall relaxation change with T and P, but the unexpected result is that, once two spectra obtained at different T and P but with the same maximum frequency $\nu_{\alpha,max}$ are compared, they completely superpose over the wide time scale investigated. That is not a trivial result, as the relaxation shape is strongly changing. Another strict check comes from Fig.2 where the logarithmic derivatives, (i.e. the slope in a log-log plot) are compared: again, the shape is identical for the same $\nu_{\alpha,max}$. Fig.2 allows a direct determination of the EW exponent γ without a fitting procedure (it is the constant value at high frequency). A summary of the dispersion change over the wide investigated range of T and P can be found in Fig.3, where β_{KWW} for the α -relaxation and EW exponent γ are plotted versus the logarithm of the α -relaxation time $\tau_\alpha=1/(2\pi\nu_{\alpha,max})$. A very nice master-curve is found for both quantities. The stretching parameter β_{KWW} was found dependent only on τ_α and to decrease (i.e. dispersion increases) as the relaxation time increases, according to the bilinear relation already found in ref.[23] (see line in Fig.3), although a limit value is attained at short τ_α . Also γ is decreasing for increasing τ_α and $\gamma(\tau_\alpha)$ is well represented by the relation $\gamma(\tau_\alpha)=K/\log(\tau_\alpha/\tau_0)$, where K is a numeric

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constant and τ_0 is the high T limiting time [24]. All these evidences tell us that EW and α -process are closely related and their dispersion is determined by τ_α . Of course this could strengthen the explanation of EW as inherent part of the α -relaxation, although the scaling proposed in ref. [17] cannot easily match $\gamma(\tau_\alpha)$.

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In order to test if such properties are common to JG relaxation, dielectric spectra of BIBE at different T and P are shown in Fig.4. In this case, loss spectra were fitted with a superposition of Fourier-transform KWW function for the α -process plus a Cole-Cole (CC) function $1/[1+(j\omega\tau)^\delta]$ for the JG relaxation. It is noteworthy that in this case, when τ_α is not so long, the α - and the JG processes are not enough separated and an apparent excess wing appears at the high frequency side. On the other hand, below T_g (or P_g), the JG peak is clearly visible. Also in the case of BIBE a perfect superposition of spectra measured at different T and P (but with the same $v_{\alpha,\max}$) is obtained. Not only the width of the α -peak is constant at constant $v_{\alpha,\max}$, but also the time scale separation of the JG process, that so appear to be closely related to the structural one and to be quite sensitive to pressure. Actually, a not perfect superposition can be noted, due to the difference of relative strength of the JG relaxation. Moreover, the presence of an additional secondary relaxation can be noted that at high frequency, insensitive to pressure and completely unrelated to structural dynamics: it was already identified as a motion of molecular sub-unit [11]. Fig.5 summarizes all these evidences: a master curve for $\beta_{\text{KWW}}(\tau_\alpha)$ is obtained, with the same variation of dispersion observed in Fig.3. Moreover, also the logarithm of the JG relaxation time $\tau_{\text{JG}} = 1/(2\pi\nu_{\text{JG}})$, if plotted vs. $\log(\tau_\alpha)$ gives a master curve, approximately linear, with a slope close to an average value of β_{KWW} . This result is in agreement with the prediction of CM (eq.1), as already found for other systems [20]. In particular, trying to calculate the time of the primitive relaxation by using eq.1, a good agreement with the JG relaxation time can be found for our system (see arrows in Fig.4). Eq.(1) is able to explain the scenario observed with DPVC, i.e. a perfect scaling of α - process and EW over different T and P range: in that case the α -peak is quite narrow and so the coupling parameter $n=1-\beta_{\text{KWW}}$ is quite small (0.29 at T_g). From eq.(1) it follows that JG and α - process are not so well separated and the former appears as an excess wing. As $n(\tau_\alpha)$, also τ_{JG} is a function only of τ_α . Although the Coupling Model seems to provide a sound explanation of the connection between α -relaxation time, dispersion (or non-exponentiality) of the α -relaxation, and the time scale of JG relaxation (including here the EW phenomenon), it does not give a strict prediction for the function $\beta_{\text{KWW}}(\tau_\alpha)$ or for the external factors causing the structural slowing down (i.e. why $\tau_\alpha=f(T\nu^y)$ or similar). On the other hand, the fact that all these three quantities are closely interrelated is one of the results predicted by the Coupling Model, that succeeded in many other applications (for a recent and more accurate description, see ref. [25]). That is very well shown by the experimental results presented here. New theories of the glass transition, or revisions of the already existing, have to face the new results that the non-exponentiality parameter β_{KWW} is invariant to different combinations of P and T keeping τ_α constant and that the time scale separation of the JG secondary relaxation from τ_α behaves in the same way.

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Conclusion

Dielectric loss spectra of the molecular glass formers DPVC and BIBE were acquired at different combination of temperature and pressure, spanning the dynamic range from melting point to glass transition. At fixed τ_α , the shape of the α -dispersion was found constant, independent of thermodynamic conditions (T and P). In other words, τ_α was found uniquely defining the dispersion. This result was not limited to the region dominated by α -peak, but also the shape of the high frequency side, dominated by excess wing or JG secondary relaxation (for DPVC and BIBE respectively), was found to be mainly dependent by the time scale τ_α , so resulting as a key parameter for the supercooled dynamics. The present results were successfully analysed in the framework of Coupling Model. In general, it has to be pointed out that all theories and models of

the glass transition should take into account the dispersion of the structural relaxation as a basic quantity to be predicted in a close relation to the behaviour of the α - and JG relaxation time scale.

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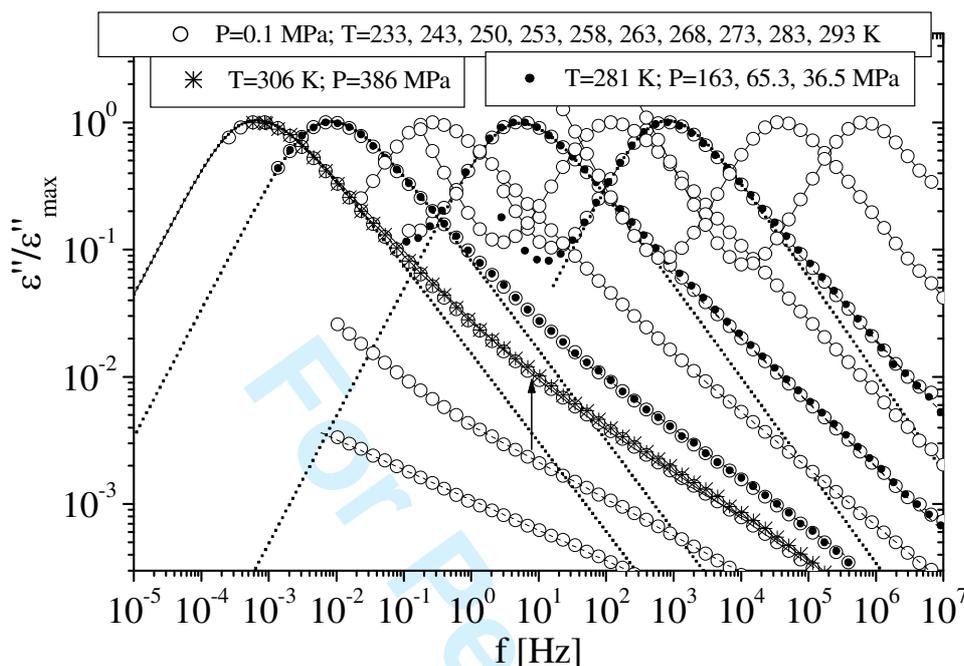


Fig.1. Normalized loss spectra of DPVC. Symbols represent experimental data (open circles from atmospheric pressure data, stars and close circles are from high pressure data). Dotted lines are from fitting KWW function ($\beta_{KWW}=0.77, 0.73, 0.71, 0.70$ from right to left). Continuous line is from fitting the total contribution. Vertical line shows the frequency related to the primitive relaxation of CM for the spectrum at 233 K and 0.1 MPa.

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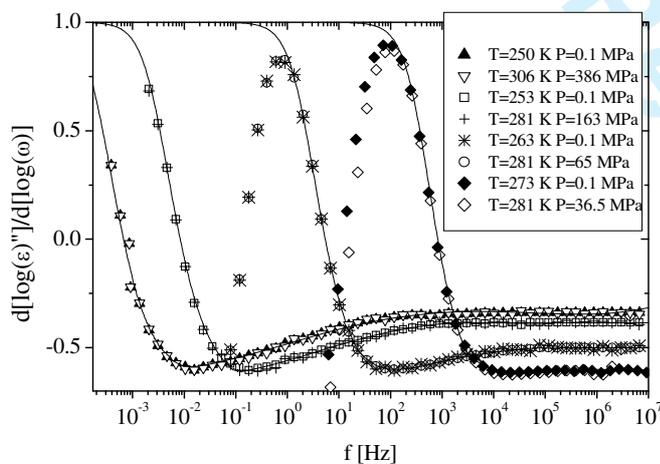


Fig.2 Bilogarithmic slopes of selected loss spectra of DPVC. Symbols represent experimental data, continuous lines the logarithmic derivatives of the total fitting contribution. Deviation at low frequencies are due to the d.c. conductivity contribution

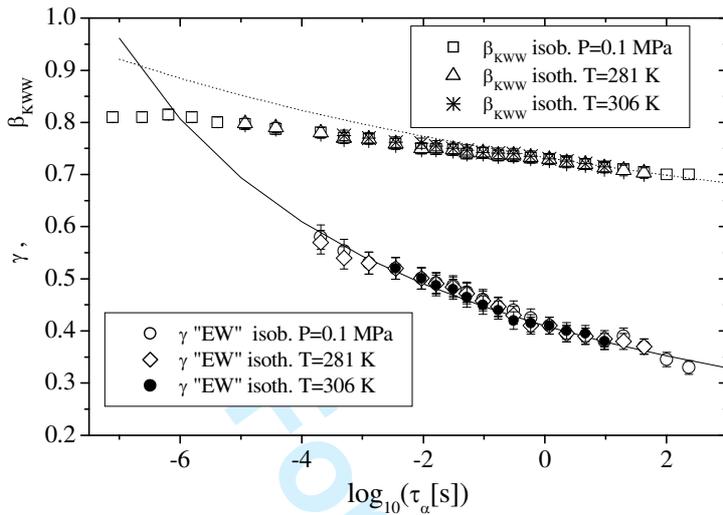


Fig. 3 DPVC: KWW parameter for the α -relaxation and γ -exponent of the excess wing contribution plotted vs. logarithm of α -relaxation time for different T and P. Symbols are from experimental data. Continuous and dotted lines are fitting functions indicated in the text.

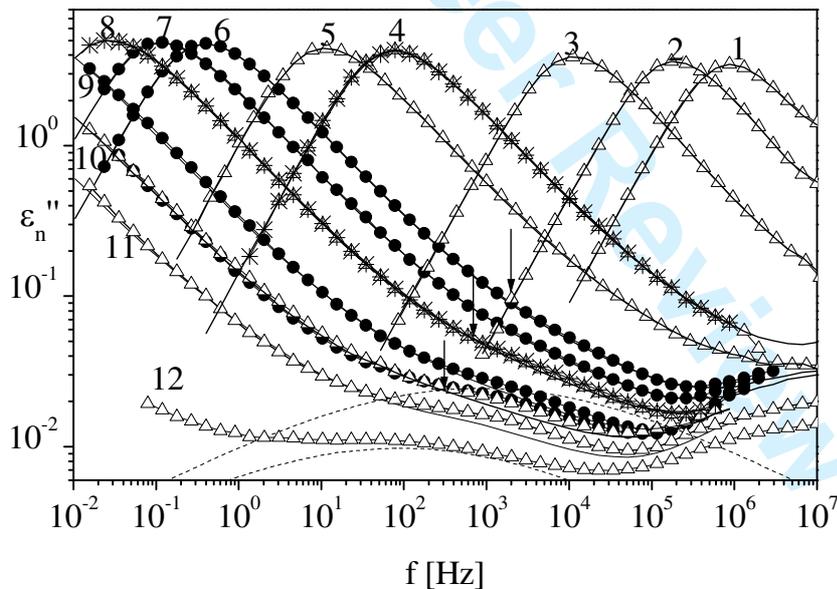


Fig. 4 Dielectric loss of BIBE at different T and P. From right to left: black lines are atmospheric pressure data at $T=271$ (1), 263 (2), 253 (3), 240 (4), 236 (5), 230 (6), 228 (7), 226 (8), 223 (9), 220.5 (10), 218 (11) K. Symbols are high pressure data; triangles: $T=278.5$ K and $P=32$ (1), 65 (2), 118 (3), 204 (4), 225 (5), 320 (8), 370 (10), 396 (11), 560 (12) MPa, circles: $T=288.2$ K and $P=350$ (6), 370 (7), 423 (9), 450 (10) MPa, stars: $T=298$ K and $P=330$ (4), 467 (8) MPa. Dashed lines are CC fitting curves. Arrows indicate the location of primitive relaxation.

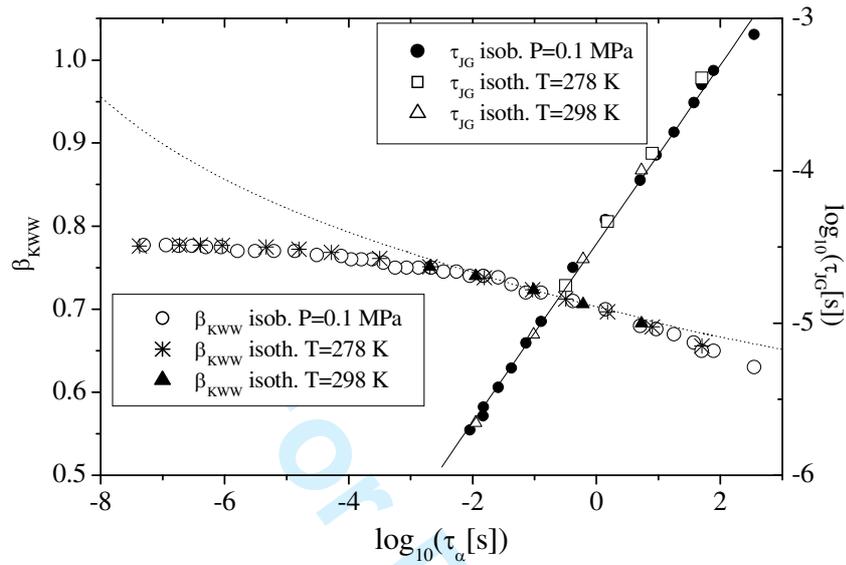
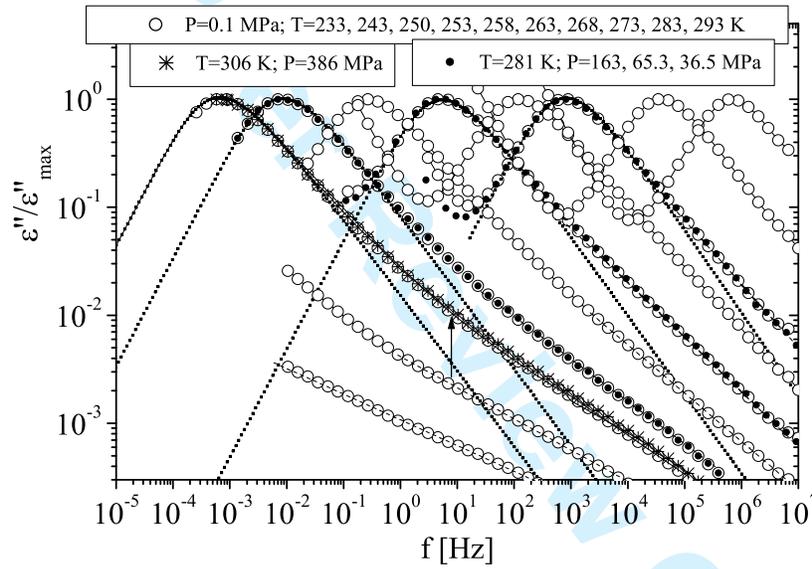
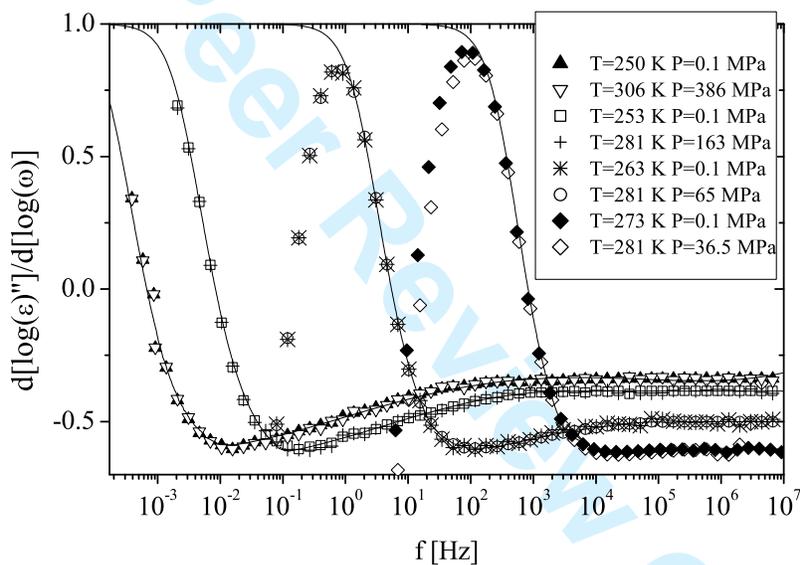


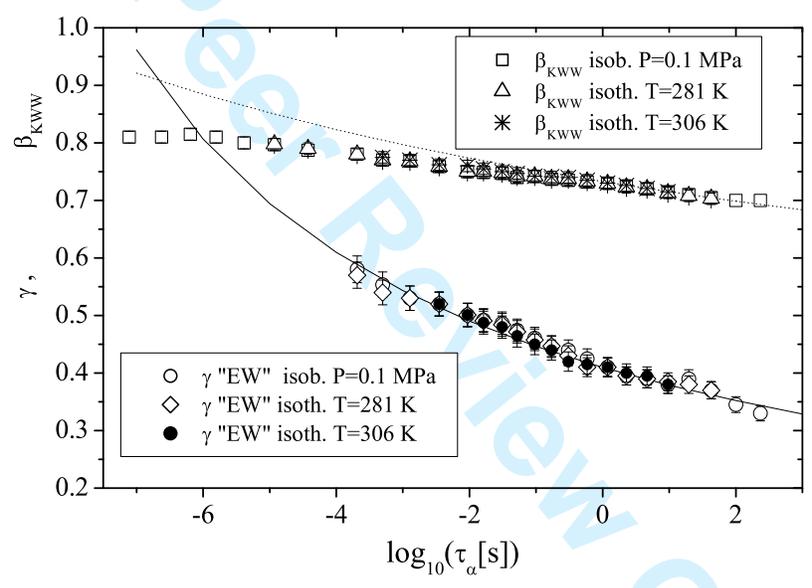
Fig. 5 - KWW parameter for the α -relaxation (left Y-axis) and logarithm of relaxation time τ_{JG} of the JG relaxation (right Y-axis) plotted vs. logarithm of α -relaxation time for different T and P. Symbol are from experimental data. Continuous and dotted lines are fitting functions indicated in text.

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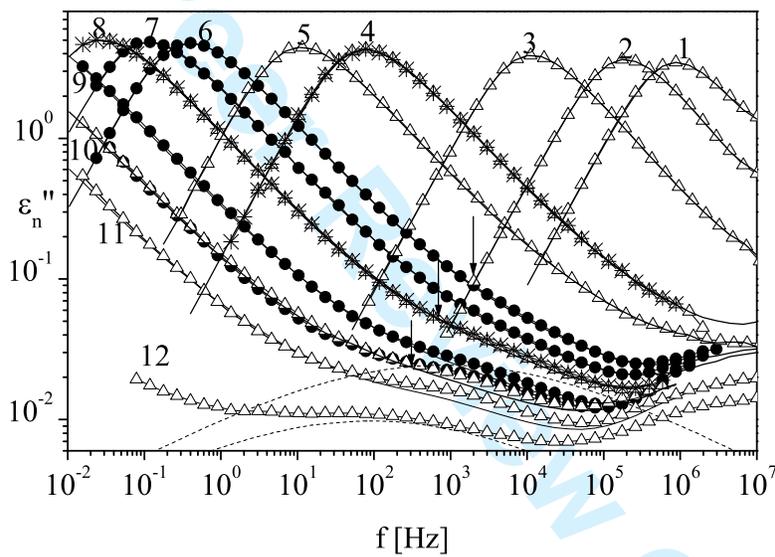




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