

# Relation between Configurational Entropy and Relaxation Dynamics of Glass-Forming Systems under Volume and Temperature Reduction

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## Abstract

The structural relaxation dynamics of two molecular glass forming systems have been analyzed by means of dielectric spectroscopy, under cooling and compression conditions. The relation of the dynamic slowing down with the reduction of the configurational entropy,  $S_C$ , as predicted by Adam and Gibbs (AG), was also investigated. As  $S_C$  is not directly accessible by experiments, it was estimated, following a common procedure in literature, from the excess entropy  $S_{exc}$  of the supercooled liquid with respect to the crystal, determined from calorimetric and expansivity measurements over the same T-P range of dynamics investigation. The AG relation, predicting linear dependence between the logarithmic of structural relaxation time and the product of temperature with configurational entropy, was successfully tested. Actually, a bilinear relation between  $S_{exc}$  and  $S_C$  was found, with different proportionality factors in isothermal and isobaric conditions. Using such results, we derived an equation for predicting the pressure dependence of the glass transition temperature, in good accordance with the experimental values in literature.

PACS codes: 64.70.Pf, 77.22.Gm, 05.70.Ce

**Keywords:** Glass transition, structural relaxation time, configurational entropy, glass transition temperature, pressure.

## 1.Introduction

According to the Adam and Gibbs (AG) model the slowing down of  $\alpha$ -relaxation time  $\tau_\alpha$  in glass-forming systems is linked to the increasing size  $N_{CRR}$  of the cooperatively rearranging regions (CRR) [1]. AG model postulates that the free energy activation barrier for a CRR relaxation is linearly increasing with  $N_{CRR}$ , that is reciprocal of configurational entropy  $S_C$  of the system. Thus, on approaching the glass transition by cooling or compressing, the reduction of configurational entropy implies a slowing down of structural dynamics, according to the equation:

$$\tau(T, P) = \tau_0 \exp\left(\frac{C_{AG}}{TS_c(T, P)}\right) \quad (1)$$

where  $\tau_0$  is the value of  $\tau$  in the limit of infinite  $(TS_c)$ , and  $C_{AG}=(s_c^* \Delta\mu/R)$ , with  $R$  the gas constant,  $s_c^*=k_B \ln 2$  and  $\Delta\mu$  is the free energy activation barrier for an elementary transition, i.e. at high temperatures where cooperativity does not take place and  $N_{CRR}=1$ . AG model is derived for an ensemble in isobaric-isothermal conditions.  $C_{AG}$  was assumed as a constant, since the increase of pressure and the decrease of temperature are believed to change only  $N_{CRR} \propto 1/S_c$ . Of course, for high compression (usually for pressures comparable than the isothermal bulk modulus, around some GPa), changes in the structure of the material could take to not negligible variations of  $\Delta\mu$ , but this is not the case of most of the experiments reported in the literature. For instance, for pressure up to 1 GPa, it has been reported that the shape of relaxation peak of a given glass-former is not depending on pressure or temperature, but only on the relaxation time [2], indication that the mechanisms of relaxation are not altered by the compression.

AG model has been criticized from the theoretical point of view, especially concerning its two main assumptions: (a) the barrier height grows like the number of molecules forming a CRR and (b) the critical configurational entropy  $s_c^*$  associated to a CRR is fixed and is equal to  $k_B \ln 2$ , independently of the size of the CRR. The first hypothesis implies that even if the number of molecules in a CRR is large, the number of configurations they can build is constant. So, a finite number of possible rearrangements in a CRR is enough to make the system relax, disregarding the volume of the CRR. When the volume is large, however, this becomes a heavy requirement that is hard to justify a priori and not obvious at all. Another objection to this hypothesis comes from ref.[3], where it is shown that in a number of glass formers if  $s_c^*$  is fixed to be  $k_B \ln 2$  the extrapolated size of the cooperatively rearranging region  $N_{CRR}$  is less than one, and if  $s_c^*$  is left as a free parameter, though constant for the whole experiment,  $N_{CRR}$  remains small. Implying that, in this view the structural cooperative relaxation is due to the simultaneous rearrangement of few molecules, contrary to what evidenced from experiments [3]. The mosaic model or "random first order transition theory" [4] allows for an alternative derivation of a generalized AG law, where a proportionality between  $\log(\tau)$  and a power law of  $(TS_c)^{-1}$  holds, without resorting to the above mentioned assumptions. Along this line, recent publications [4, 5, 6] provide careful and physically reasonable revisions of AG model and predictions. In spite of this shortcomings, the Adam-Gibbs relation (Eq.1) succeeded quite well in accounting for experimental data and gained a considerable popularity. In fact, Eq.(1) has been successfully applied to reproduce the dynamics of supercooled liquids above the glass transition in many cases, both in numerical simulations [7, 8, 9] and experiments [10, 11, 12, 13, 14, 15 and references therein]. For molecular dynamics simulations, the determination of configurational entropy  $S_C$  is directly obtained from the difference of the total entropy and the vibrational entropy of typical basins sampled,  $S_{vib}$  or by the distribution of energy minima in energy landscape. Anyway, the good

agreement found between Eq.(1) and data of molecular dynamics simulations is puzzling, as the relaxation is there investigated on a very short timescale (ns-ps) where the cooperativity should not be so important. Other doubts can be raised about the correct decomposition between vibrational and configurational modes in a liquid at this short time-scale, rather than in a solid, as a vibration inside a definite cage cannot be precisely defined for a liquid.

Concerning experiments, since  $S_{vib}$  is not directly accessible, a common approximation for  $S_C$  in literature is to calculate the excess entropy  $S_{exc}$  of the supercooled liquid with respect to the crystal. This approximation gave rise to several criticisms [16]. The main one is that the vibrational properties of a crystal are different from that of the supercooled liquid at the same T-P conditions and so a vibrational excess term is considerably contributing to  $S_{exc}$  [16]. As in supercooled liquids a relation  $\log[\tau(T,P)] \propto [TS_{exc}(T,P)]^{-1}$  is usually fulfilled [12, 13, 14, 15], a hypothesis about the proportionality  $S_{exc} \propto S_C$  was proposed, yielding again the relation of Eq. (1) [7, 17, 18]. Notwithstanding the above mentioned results appear as convincing tests of the AG model, the debate is still open about several issues: (a) the right way of calculating the configurational entropy in an experiment [16, 19, 20, 21]; (b) the physical meaning of the size of a CRR [21, 22, 23, 24]; (c) the amount of configurational part of  $S_{exc}$  [7, 17, 16, 25, 21, 26, 27, 28, 18]; (d) the independence from pressure and temperature of the coefficient  $C_{AG}$  in Eq. (1) [11, 13, 14, 29, 8, 9]. Our previous experimental studies confirmed that AG relation is fulfilled also at high pressure [11, 13, 14]: so a proportionality can be postulated between  $S_{exc}$  and  $S_C$  or, better, a bilinear relation, with different proportionality factors  $g_T(P)$  and  $g_P(T)$  in isobaric and isothermal conditions respectively [30] (see Eq. (2) below). As required by general principle of thermodynamic, configurational entropy must be a function of state and therefore  $g_T(P)$  and  $g_P(T)$  are mutually dependent. In particular, when  $S_C(T,P)$  is calculated along an isobaric path at atmospheric pressure,  $P_{atm}$ , from the initial temperature  $T_K$  till the

final temperature  $T$ , followed by an isothermal path at  $T$  till the final pressure  $P$ , the configurational entropy is expressed by:

$$S_c(T, P) = g_T(P_{atm}) \int_{T_K}^T \frac{\Delta C_p}{T'} dT' - g_P(T) \int_{P_{atm}}^P \Delta \left( \frac{\partial V}{\partial T} \right)_{P'} dP' \quad (2)$$

where  $T_K$  is defined as the temperature where  $S_c(T_K, P=0.1 \text{ MPa})=0$ ,  $(\Delta C_p/T)dT=[(C_p^{\text{melt}} - C_p^{\text{cryst}})/T]dT$  and  $\Delta(\partial V/\partial T)_P dP = -[(\partial V/\partial T)_P^{\text{melt}} - (\partial V/\partial T)_P^{\text{cryst}}]dP$ , are the excess heat capacity and the temperature derivative of the excess volume of the melt with respect to the crystal. The derivation of Eq. (2) is valid for systems in thermodynamic equilibrium (i.e. above the glass transition) and cannot be used for systems in the glassy state. Further details about such derivation and the compatibility with thermodynamic requirements for a function of state can be found in ref. [30]. Previous applications of Eq.(2) to represent set of isobaric data in molecular and polymeric glass-formers can be found in ref. [30, 32, 33]. The present experimental study comprises an extensive study of dynamics under isothermal compression of two glass formers: diphenyl-vinylene carbonate and polyphenylglycidylether, already partially studied [34, 35, 31, 36]. Moreover, using the above mentioned procedure,  $S_{exc}$  is calculated from calorimetric and expansivity measurements over a wide T-P range, allowing a direct comparison with the dielectric relaxation times  $\tau_\alpha$  and a succesful test of the AG model. In particular we show that  $\log[\tau(T,P)]$  is proportional to  $[TS_c(T,P)]^{-1}$  and the proportional coefficient is constant for low-pressure values. Moreover, from our procedure, we derive a general expression for predicting from configurational entropy the values for the pressure dependence of the glass transition temperature in the limit of low pressure.

## 2. Experimental procedures

Diphenyl-vinylene carbonate (DPVC) and polyphenylglycidylether (PPGE) were obtained from Aldrich. Their molecular weight is  $348.15 \text{ g mol}^{-1}$  (DPVC) and  $345 \text{ g mol}^{-1}$  (PPGE). The

glass transition temperature  $T_g$ , obtained by DSC (onset), is 251 K for DPVC and 258 K for PPGE. Dielectric measurements, both at atmospheric and at high pressure, were carried out using a Novocontrol Alpha-Analyzer ( $\nu=10^{-3}$ - $10^7$  Hz). For atmospheric pressure measurements, a parallel plate capacitor separated by a quartz spacer (geometric capacitance  $\sim 90$  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  $\sim 30$  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 able to reach 700 MPa. The high pressure chamber was surrounded by a metallic jacket, whose temperature was varied in the interval 200–360 K and controlled within 0.1 K by means of a thermally conditioned liquid flow. Dielectric measurements were performed after equilibrating temperature and pressure for enough time to have data in thermodynamic equilibrium (at least 30 minutes or more, up to 4 times the relaxation time  $\tau$ , on approaching the glass transition). PVT data were obtained by GNOMIX high pressure dilatometer, while absolute density measurements, at ambient temperature, were made using a helium pycnometer. Calorimetric data were obtained using a Mettler 30 Differential Scanning Calorimeter.

### 3. Results

The relaxation map of structural relaxation time of DPVC in isobaric and isothermal conditions is shown in Fig.1(a)-(b), respectively. The Vogel-Fulcher-Tamman (VFT) function fitting the data at 0.1 MPa has the parameters:  $\log_{10}(\tau_0/s)=-18.6\pm0.4$ ,  $B=1200\pm50$  K and the Vogel temperature  $T_0=193\pm5$  K. The dielectric glass transition, defined as the temperature at which  $\log_{10}(\tau/s)=2$ , is 251 K and the steepness index  $m=d[\log_{10}(\tau)]/d[T_g/T]|_{T_g}=89$ . The isothermal scans show the linear relation  $\log_{10}(\tau)\propto(P\Delta V^\#)/RT$ , where  $\Delta V^\#$  is the so-called

activation volume, that is decreasing with temperature:  $\Delta V^\# = 240 \pm 15 \text{ cm}^3 \text{ mol}^{-1}$  at  $T = 271 \text{ K}$  and  $\Delta V^\# = 170 \pm 10 \text{ cm}^3 \text{ mol}^{-1}$  at  $T = 306 \text{ K}$ . From the extrapolation of the linear behavior it is possible to estimate the value  $T_g(P)$ . It is increasing with pressure as a second order polynomial, but at low pressure it has a slope  $dT_g(P)/dP = 190 \text{ K GPa}^{-1}$ .

Similar considerations are valid also for data of PPGE shown in Fig.2-(a)-(b). The VFT function fitting parameters can be found in refs.[13, 35, 36]. Fit of data at 0.1 MPa have the parameters:  $\log(\tau_0/s) = -15.1 \pm 0.2$ ,  $B = 708 \pm 10 \text{ K}$  and the Vogel temperature  $T_0 = 217 \pm 2 \text{ K}$ . At times shorter than  $0.1 \text{ } \mu\text{s}$  times deviates from the VFT behavior, according to a crossover behavior often reported in literature [12]. The dielectric glass transition is  $256 \text{ K}$  and the steepness index  $m = 107$ . The isothermal scans show a non-linear relation between logarithm of times and pressure, of the kind  $\log(\tau) \propto B/(P_0 - P)$ . A deviation from the linear behavior is expected for a wide pressure range, but the pressure value at which the non-linearity takes place is material dependent. Usually the non linearity shows up at lower pressure for systems with higher  $m$  index. From the extrapolation of the non-linear behavior of  $\log_{10}(\tau/s)$  to 2 it is possible to estimate the value  $T_g(P)$ . It is increasing with pressure as a second order polynomial, but at low pressure it has a slope  $dT_g(P)/dP = 154 \text{ K GPa}^{-1}$ .

PVT data and thermograms of DPVC and PPGE are not reported for lack of space and a detailed description about this procedure will be published elsewhere [53]. Anyway, expansivity and calorimetry data of PPGE are reported partially in refs. [34, 35, 36]. For PPGE the specific heat was measured in both liquid and crystalline state. On the other hand, the temperature derivative of the volume of the crystal of PPGE was not available, and it was obtained from that of the glassy state. In fact, the data of the few systems reported in literature [50] suggest that the temperature derivative of specific volume in the glassy state is not more than 15% higher than in the crystalline one. Since in the supercooled liquid  $(\partial V/\partial T)$  is nearly 3 times higher than that in the crystal phase at the same temperature, the

error in estimating the excess expansion (and then the term  $\Delta(S_{exc})_{isoth}$ ) using the glassy value instead of the crystalline one is negligible (less than 5%). For DPVC all the thermodynamic data used in the present paper are obtained directly from the comparison of supercooled and crystalline state in the same range of the dielectric measurements. In this case, no fitting procedure was applied: isothermal and isobaric reduction of excess entropy (the two terms in Eq.(2)) were obtained by interpolating and integrating the data. Excess entropy of DPVC is well represented by the function  $S_{exc}=S_{\infty}(1-T_K/T)$ , with  $S_{\infty}=130\pm1 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $T_K=198.7\pm0.8 \text{ K}$ . Specific volume of DPVC is well represented by Tait equation  $V=V_0(1-0.094\ln(1+P/B(T)))$ , where  $V_0=1.0023+6.16\cdot10^{-4}(T(^{\circ}\text{C}))+4.22\cdot10^{-7}(T(^{\circ}\text{C}))^2 \text{ cm}^3/\text{g}$  and  $B=229\cdot\exp(-3.95\cdot10^{-3}(T(^{\circ}\text{C}))) \text{ MPa}$ . The temperature derivative of the volume of the crystal was estimated to be  $(\partial V/\partial T)_P^{\text{cryst}}=1.79\cdot10^{-4} \text{ cm}^3\text{g}^{-1} \text{ K}^{-1}$ , only slightly changing with  $P$  ( $\partial \ln[(\partial V/\partial T)_P^{\text{cryst}}]/\partial P \sim 0.6 \text{ GPa}^{-1}$ ). Using these data the isothermal reduction of entropy

$$\Delta(S_{exc})_{isoth} = - \int_{P_{atm}}^P \Delta\left(\frac{\partial V}{\partial T}\right)_{P'} dP' \text{ can be calculated according to Eq.(2). If Eq.(1) is valid at any}$$

pressure, and  $C_{AG}$  does not change with pressure as postulated in section 1, it is possible to obtain an expression for the “dynamic” configurational entropy,  $S_C^{DYN}$ , i.e. the value of configurational entropy fulfilling AG relation:

$$S_C^{DYN} = \frac{C_{AG}}{T \ln(\tau(T, P)/\tau_0)} \quad (3)$$

where  $\tau_0$  and  $C_{AG}$  are fixed to the values obtained at  $P=0.1 \text{ MPa}$ . The test on isothermal data is indeed a direct check of Eq.(2). This test is shown in Fig.3-(a)-(b) for DPVC and PPGE respectively. Dynamic data are corresponding to those in Fig.1-(b) and Fig.2-(b).

A proportionality between  $S_C^{DYN}$  and  $\Delta(S_{exc})_{isoth}$  is found, as expected when the bilinear relation of Eq.(2) is valid. The slope is equal to the ratio  $g_P(T)/g_T(P_{atm})$ . From these data, it results that  $g_P(T)$  changes negligibly with  $T$ . Moreover the ratio  $R=g_P(T)/g_T(P_{atm})$  is always



bigger than 1.  $R$  is  $1.44 \pm 0.04$  for DPVC and  $1.35 \pm 0.15$  for PPGE. The two functions  $g_T(P)$  and  $g_P(T)$  are expected to be different because isobaric changes include configurational, harmonic, and anharmonic terms of the potential energy, whereas isothermal ones, depending on the expansivity, have no contribution from the harmonic term of the potential energy [37, 32]. If  $R$  was 1, the expression in Eq. (2) would reduce to that originally proposed by AG or to that proposed by Angell and Borick [17] for  $g_T = g_P = \text{const}$  different from unity. In our case we have that  $g_T(P_{\text{atm}})/g_P(T) = 0.70 \pm 0.02$  for DPVC and  $0.74 \pm 0.08$  for PPGE, that seems to suggest that isothermal reduction of excess entropy is much more effective in term of reduction of configurational entropy. Similar values of  $g_T(P_{\text{atm}})/g_P(T) \approx 0.7$  have been found for the glass-forming van der Waals molecular liquids OTP and TPCM [30]. It is to be pointed out that our procedure estimates only the ratio of these two quantities and it is not possible to claim what is the fraction of the excess entropy that is configurational, differently from what stated in ref. [25].

#### 4. Discussion

Following our approach, Eq.(2) can be represented in this case as a bilinear equation, where the parameter  $g_P(T)/g_T(P_{\text{atm}})$  is constant, determined by the plot of isothermal data in Fig.3. In this way, taking into account the relative reduction of configurational entropy under pressure, it is possible to determine a “corrected” excess entropy,  $S_{\text{exc}}^C$ , i.e. a quantity that is always proportional to the true configurational entropy:

$$S_C(T, P) = g_T(P_{\text{atm}}) S_{\text{exc}}^C(T, P) \quad (4.a)$$

$$S_{\text{exc}}^C(T, P) = S_{\text{exc}}(T, P_{\text{atm}}) - \frac{g_P(T)}{g_T(P_{\text{atm}})} \int_0^P \frac{\partial(\Delta V)}{\partial T} dP' \quad (4.b)$$

Eq.(1) can be expressed by using the new quantities as:

$$\log(\tau(T, P)) = \log \tau_0 + \log e \frac{C_{AG}}{g_T(P_{atm})} [TS_{exc}^C(T, P)]^{-1} \quad (5)$$

in the case  $g_P(T)/g_T(P_{atm}) \approx 1$  configurational entropy can be replaced by excess entropy.

$S_{exc}^C$  was calculated for DPVC and PPGE, by using the respective values for  $g_P(T)/g_T(P_{atm})$  obtained from isothermal data. Fig.4 shows the test of Eq.(5) for data in isobaric (for PPGE) and isothermal (for DPVC) conditions. The data of the two systems collapse in two master-curves, showing the linear behavior predicted by Eq.(1). We postulated the invariance of  $\tau_0$  and  $C_{AG}$  on pressure, so it is true that such result is partially expected but the master-plot of Fig.4 is possible only because the bilinear relation between configurational entropy and excess entropy of the melt with respect to the crystal expressed by Eq.(2) holds. Moreover, for each system, the data measured in different isobaric conditions fall into one single master curve: that is resulting from the fact that the ratio  $g_P(T)/g_T(P_{atm})$  assumes a single value independent of temperature.

The independence on pressure of  $C_{AG}$  and  $\tau_0$  is consistent to data in Fig.4. In previous analyses these two parameters were usually assumed as pressure-independent (for example Refs. [12, 13, 14, 15, 30]), but never checked. It is to be reminded that in AG model the energy barrier  $C_{AG}$  should be not dependent on pressure, as long as the effective barrier for a CRR is increasing as  $C_{AG}/S_C$ , while configurational entropy is reducing.

Starting from this speculation recently the assumption of  $C_{AG}=\text{const.}$  was questioned and the test of the AG were retained misleading [29]. In the present work we clearly demonstrate that at least in the low-pressure regime, i.e. for  $P < 300$  MPa in the case of DPVC and PPGE, this dependence is negligible. In fact, for each system the slope of the curve  $\log[1/\tau(T, P)]$  vs  $1/(TS_{exc}^C)$  for different isobaric condition is the same, meaning that  $C_{AG}$  is the same. Noteworthy, our finding agrees with previous results obtained by numerical simulations

reporting a negligible variation of  $C_{AG}$  with pressure for density changes up to the order of 20% [8, 9] (the larger density variations in our measurements are of the order of 5-8%).

It is important to note that sometimes an incorrect evaluation of  $S_c(T,P)$  can lead to an incorrect evaluation of the behaviour of  $C_{AG}$ , as well as of  $\tau_0$ . For example, if we consider  $S_c(T,P) \propto S_{exc}(T,P)$  ( $g_T = g_P = \text{constant}$ ) and  $\log[1/\tau(T,P)]$  is plotted as a function  $(TS_{exc})^{-1}$ , we can find again a linear behaviour, but we do not find a master curve describing the data in different isobaric conditions (an example for PPGE is in Fig.5). From a least squares linear fit of the data of PPGE at different isobaric conditions from 0.1 to 240 MPa, we obtain  $\log(\tau_0/s) \approx -15.7$  and  $C_{AG}/g_T(P_{atm})$  changing from 45 to 56 kJ mol<sup>-1</sup> (see inset Fig.5). This approach gives fitting curves completely consistent to the data, but the energy barrier is found to change too much (more than 25%) for density changes around 5%. Similar density effects should be relevant already even for cooling at ambient pressure. Summarizing, fitting the relation  $\log[1/\tau(T,P)]$  versus  $(TS_{exc})^{-1}$  with a  $C_{AG}$  dependent on pressure is possible, but the results are not in agreement with the physical meaning of the quantities involved in AG model. On the other hand, assuming a negligible dependence of  $\log\tau_0$  and  $C_{AG}$  on pressure, at least for very low pressure, is quite natural. Moreover, by estimating the ratio between excess and configurational entropy under isothermal reduction, a straightforward method to calculate  $S_{exc}^C$  allows the construction of the master-curve predicted by Eq.(1).

However the present study shows how, from the experimental point of view, the AG equation could represent very well the data with  $C_{AG}(P)$  strongly changing with pressure or, alternatively, with a bilinear relation between excess and configurational entropy. Choosing one option rather than the other is just a matter of belief and of general considerations and it cannot come unequivocally from the present experimental data. We prefer the bilinear approach since it gives a master-curve of the data (Fig.4). Moreover, there is a physical reason to rationalise the result, since a different proportionality between the reduction of excess and

configurational entropy is expected if such reduction is performed isothermally or isobarically. In fact, the vibrational contribution of the excess entropy should change less under isothermal compression than under isobaric cooling. On the other hand, this does not exclude the other possibility.

From Eq.(1) it is possible to calculate the pressure dependence of the glass transition temperature,  $T_g$ , defined such as the isochronal locus where  $\tau(P, T_g(P))=100$  sec. According to the AG model, T-P couples of values corresponding to the condition  $\tau(P, T_g(P))=100$  sec are those satisfying the condition  $(TS_c)=\text{const}$ . Solving the equation  $d(TS_c)_{T_g}=0$  with Eq.(2) we obtain that in the low P limit the pressure dependence of the glass transition temperature can be described by:

$$\left. \frac{dT_g}{dP} \right|_{P_{atm}} = \frac{-T_g \left( \frac{\partial S_c}{\partial P} \right)_T}{S_c + T_g \left( \frac{\partial S_c}{\partial T} \right)_P} \approx \left[ \frac{T_g (V_g \Delta \alpha)}{S_{exc}(T_g) + \Delta C_p(T_g)} \right] \cdot \frac{g_P(T_g)}{g_T(P_{atm})} = X \cdot \frac{g_P(T_g)}{g_T(P_{atm})} \quad (6)$$

where  $V_g$  is the specific volume of the glass,  $\Delta \alpha$  the excess expansivity, and  $\Delta C_p$  excess heat capacity calculated at the glass transition at ambient pressure.

In Fig.6 experimental values of  $dT_g/dP$  at ambient pressure,  $dT_g/dP|_{P=atm}$  for DPVC and PPGE, are compared with those predicted by the theory (Eq. (6)), using the values of  $g_P(T)/g_T(P_{atm})$  found from the analysis of relaxation time data. A good agreement is obtained. Moreover, the value of  $dT_g/dP|_{P=atm}$  is reported in literature for many systems, and the comparison between the experimental value and that calculated through Eq.(6) can be another way to test AG model. Actually such comparison was considered in literature to test the validity of different theories of the glass transition [38, 39, 40, 41, 42]. Also the AG theory was tested with this procedure, but considering that  $S_c(T, P) \propto S_{exc}(T, P)$ . As the ratio  $g_P(T)/g_T(P_{atm})$  is different than 1, this assumption led to an incorrect evaluation of  $dT_g/dP|_{P=atm}$  and consequently to sometimes incorrect conclusion [38, 39]. In Fig.6 the experimental values of  $dT_g/dP|_{P=atm}$  of

several glass-formers are plotted versus the quantity  $X$ , obtained from thermodynamic data from literature [42, 43, 44]. There is a fairly good agreement, with the two quantities roughly proportional, and a proportionality constant in the range where usually  $g_p(T)/g_T(P_{atm})$  is found. This further result confirm that AG model, despite many weak points, is able to describe experimental data of glass formers. The introduction of Eqs. (4) for the calculation of configurational entropy makes possible a fully consistent analysis of the relaxation behavior.

## 5. Conclusion

In this paper we proposed a straightforward test of the AG model for the glass transition. The analysis was performed on two molecular glass-formers, DPVC and PPGE. These systems are suitable for this type of analysis since we know their thermodynamic and dynamic data in the same (T,P) interval, so that  $S_c(T,P)$  can be calculated in the same interval of  $\tau(T,P)$  without the necessity of any extrapolation procedure. First, we compared the isothermal reduction of excess entropy (Fig.3) to what should be expected from AG model for  $\tau(T,P)$ . The quantity  $S_C^{DYN} = C_{AG}/T \ln(\tau(T,P)/\tau_0)$  should shift linearly with the isothermal reduction of excess entropy only if AG model is valid and we found directly such proportionality for a wide range of pressures and temperatures and for both systems. So AG prediction, i.e. the inverse of logarithm of relaxation time proportional to  $1/(TS_{exc})$ , was found valid. On the other hand, our test evidenced that the slope was not 1, as expected, but higher: the proportionality constant is therefore different if the entropy is reduced isothermally rather than isobarically. As a second approach, we followed the suggestion of ref. [29], that, criticizing AG test to pressure data, postulated a variation of the proportionality constant  $C_{AG}$  with pressure. Surprisingly we found (Fig.6) a linear behaviour between  $\log[1/\tau(T,P)]$  and  $(TS_{exc})^{-1}$ , but with a slope  $C_{AG}/g_T(P_{atm})$  strongly pressure dependent. Such a variation, at least for moderate pressure, would be in contrast with the assumption of original AG model, where

the activation energy was assumed to increase with the CRR size and the free energy barrier  $\Delta\mu$  was taken as constant. Of course, such assumption may be contradict by the present results. Summarising, the AG model - in conjunction with the conventional assumption that excess and configurational entropy are identical or strictly proportional- is disproved by the present paper. On the other hand, a linear behavior can still be found between  $\log[1/\tau]$  and  $(TS_{\text{exc}})^{-1}$  along isobaric or isothermal path variations, but with different proportionality constants. The AG model can be so preserved only if a bilinear relation between excess and configurational entropy is considered or if a strong pressure dependence of activation barrier  $C_{\text{AG}}$  is allowed even for small density variations. This last condition is at odds with the assumptions of the original AG model [1] and with the results of recent numerical simulations [8, 9]. Moreover, by using the bilinear approach and the calculation of  $S_c$  by Eqs. (4), from the AG equation we can calculate values of  $dT_g/dP|_{P=\text{atm}}$  in agreement with the experimental ones. Summarizing, a careful comparison of the pressure dependence of relaxation time with the isothermal reduction of excess entropy allows a direct check of the AG model. The procedure shown here can be extended to any other systems where thermodynamic and dynamic data are obtained in the same range close to the glass transition at different pressures and temperatures.

## Acknowledgments

Andreas Best (Max Planck Institute for Polymer Research, Mainz) is acknowledged for the assistance in getting expansivity and calorimetry data of DPVC. Financial support by MIUR-FIRB 2003 D.D.2186 grant RBNE03R78E is kindly acknowledged.

## References

- [1] G. Adam, J.H. Gibbs, J. Chem. Phys. 28 (1965) 139.
- [2] K.L. Ngai, R. Casalini, S. Capaccioli, M. Paluch, C.M. Roland, J. Phys. Chem. B 109 (2005) 17356
- [3] G. P. Johari, J. Chem. Phys. 112 (2000) 8958
- [4] T. R. Kirkpatrick, D. Thirumalai, P.G. Wolynes, Phys. Rev. A 40 (1989) 1045
- [5] J. P. Bouchaud and G. Biroli, J. Chem. Phys. 121 (2004) 7347
- [6] V. Lubchenko and P.G. Wolynes, Ann. Rev. Phys. Chem. 58 (2007) 233
- [7] L.M. Martinez, C.A. Angell, Nature 410 (2002) 663.
- [8] A. Scala, F.W. Starr, E. La Nave, F. Sciortino, H.E. Stanley, Nature 406 (2000) 166.
- [9] S. Sastry, Nature 409 (2001) 164.
- [10] D. Cangialosi, A. Alegria, J. Colmenero, J. Chem. Phys. 124 (2006) 024906
- [11] S. Capaccioli, M. Lucchesi, R. Casalini, S. Presto, P.A. Rolla, M.T. Viciosa, S. Corezzi, D. Fioretto, Phil. Mag. B 82 (2002) 651.
- [12] R. Richert, C.A. Angell, J. Chem. Phys. 108 (1998) 9016.
- [13] R. Casalini, S. Capaccioli, M. Lucchesi, P.A. Rolla, S. Corezzi, Phys. Rev. E 63 (2001) 031207.
- [14] R. Casalini, S. Capaccioli, M. Lucchesi, P.A. Rolla, M. Paluch, S. Corezzi, D. Fioretto, Phys. Rev. E 64 (2001) 041504.
- [15] R. Casalini, M. Paluch, J.J. Fontanella, C.M. Roland, J. Chem. Phys. 117 (2002) 4901.
- [16] G.P. Johari, J. Non-Cryst. Solids 307-310 (2002) 387; J. Chem. Phys. 112 (2000) 8958; J. Chem. Phys. 116 (2002) 387.
- [17] C.A. Angell, S. Borick, J. Non-Cryst. Solids 307-310 (2002) 393.
- [18] C. A. Angell, Y. Yue, L.-M. Wang, J. R. D. Copley, S. Borick, and S. Mossa, J. Phys.: Condens. Matter 15 (2003) S1051.
- [19] G.P. Johari, J. Phys. Chem. B 105 (2001) 3600.

- [20] R.J. Speedy, J. Phys. Chem. B 103 (1999) 4060.
- [21] O. Yamamuro, I. Tsukushi, A. Lindqvist, S. Takahara, M. Ishikawa, T. Matsuo, J. Phys. Chem. B 102 (1998) 1605.
- [22] K.L.Ngai, J. Phys. Chem. B 103 (1999) 5895-5902
- [23] H. Huth, M. Beiner and E. Donth, Phys. Rev. B 61 (2000) 15092
- [24] D. Cangialosi, A. Alegria, J. Colmenero Phys. Rev. E 76 (2007) 011514 ; D. Cangialosi, A. Alegria, J. Colmenero, J. Chem. Phys. 128 (2008) 224508.
- [25] S. Corezzi, L. Comez, D. Fioretto, Eur. Phys. J. E 14 (2004) 143.
- [26] L.-M. Wang and R. Richert, Phys. Rev. Lett. 99 (2007) 185701.
- [27] W. A. Phillips, U. Buchenau, N. Nücker, A.-J. Dianoux, and W. Petry, Phys. Rev. Lett. 63 (1989) 2381.
- [28] G. P. Johari, J. Chem. Phys. 126 (2007) 114901.
- [29] G. P. Johari, J. Chem. Phys. 119 (2003) 1.
- [30] D. Prevosto, M. Lucchesi, S. Capaccioli, R. Casalini, P.A. Rolla, Phys. Rev. B 67 (2003) 17420; D. Prevosto, S. Capaccioli, M. Lucchesi, P.A. Rolla, R. Casalini, Phys. Rev. B 71 (2005) 136202.
- [31] S. Corezzi, M. Beiner, H. Huth, K. Schroter, S. Capaccioli, R. Casalini, D. Fioretto, E. Donth, J. Chem. Phys. 117 (2002) 2435–2448; S. Corezzi, Ph.D. Thesis, University of Perugia, Perugia, Italy, 2003.
- [32] D. Prevosto, S. Capaccioli, M. Lucchesi, P.A. Rolla, J. Non-Cryst. Solids 351 (2005) 2611.
- [33] D. Prevosto, S. Capaccioli, M. Lucchesi, D. Leporini, P.A. Rolla, J. Phys.: Condens. Matter 16 (2004) 6597.
- [34] S. Capaccioli, M. Lucchesi, D. Prevosto, R. Casalini, P.A. Rolla, Phil. Mag. B 84 (2004) 1513.



- [35] S. Capaccioli, D. Prevosto, K. Kessairi, M. Lucchesi, P.A. Rolla *Phil. Mag. B* 87 (2007) 681.
- [36] S. Capaccioli, G. Ruocco, F. Zamponi, *J. Phys. Chem. B* 112 (2008) 10652 and references therein.
- [37] K. Huang, *Statistical mechanics* (1987, John Wiley & Sons)
- [38] M. Goldstein, *J. Appl. Phys.* 46 (1975) 4153.
- [39] C.A. Angell, W. Sichima, *Ann. N.Y. Acad. Sci.* 279 (1976) 53.
- [40] E. Williams, C.A. Angell, *J. Phys. Chem.* 81 (1977) 232.
- [41] C.A. Angell, E. Williams, K.J. Rao, J.C. Tucker, *J. Phys. Chem.* 81 (1977) 238.
- [42] T. Atake, C.A. Angell, *J. Chem. Phys.* 83 (1979) 3218.
- [43] M. Pietralla, P. Mayr, K. Weishaupt, *J. Non-Cryst. Solids* 195 (1996) 199.
- [44] G. Fytas, A. Patkowski, G. Meier, Th. Dorfmueller, *J. Phys. Chem.* 80 (1984) 2214.
- [45] R. L. Cook, J. H. E. King, C. A. Herbst, and D. R. Herschbach, *J. Chem. Phys.* 100 (1994) 5178
- [46] S. Takahara, O. Yamamuro, and H. Suga, *J. Non-Cryst. Solids* 171 (1994) 259
- [47] A. Gilchrist, J. E. Earley, and R. H. Cole, *J. Chem. Phys.* 26 (1957) 196
- [48] D. W. Van Krevelen, *Properties of Polymers* (1997, Elsevier: Amsterdam)
- [49] R. Casalini, M. Paluch, and C. M. Roland, *J. Phys. Chem. A* 107 (2003) 2369
- [50] M. Naoki, H. Endou, K. Matsumoto, *J. Phys. Chem.* 91 (1987) 4169; Expansion data: M. Naoki, S. Koeda, *J. Phys. Chem.* 93 (1989) 948.
- [51] M. Naoki, M. Seki, H. Kugo, F. Saito, T. Tanioka, *J. Phys. Chem.* 95 (1991) 5628.
- [52] M. Naoki, T. Tanioka, K. Karasawa, A. Kinoshita, *J. Chem. Phys.* 94 (1991) 8342.
- [53] A. Best, S. Capaccioli in preparation
- [54] M. Paluch, R. Casalini, A. Best, A Patkowski, *J. Chem. Phys.* 117 (2002) 506241

[55] C. M. Roland, S. Hensel-Bielowka, M. Paluch, and R. Casalini, Rep. Prog. Phys. 68 (2005) 1405.

## Figure Captions

Fig.1 Logarithm of relaxation time as a function of (a) the inverse of temperature or (b) pressure for DPVC (solid and open symbols respectively). Lines are VFT fit for (a) and linear regression for (b).

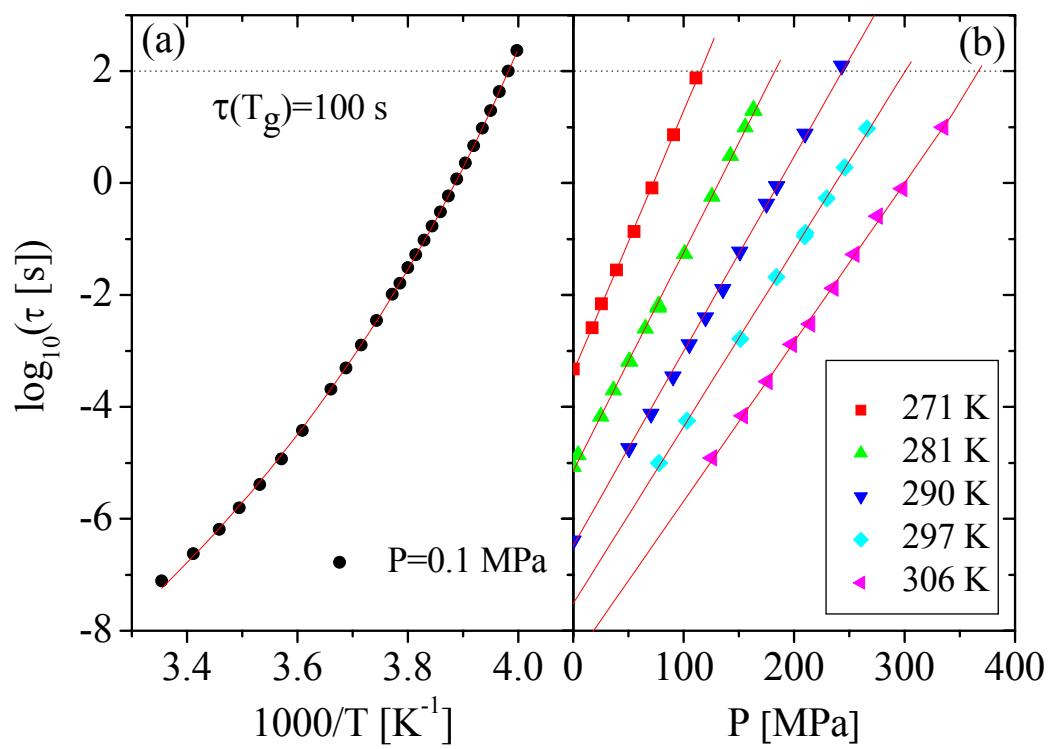
Fig.2 Logarithm of relaxation time as a function of (a) the inverse of temperature or (b) pressure for PPGE (solid and open symbols respectively). Lines are VFT fits.

Fig.3. (a) Plot of  $S_C^{DYN}$  (Eq.3) versus  $\Delta(S_{exc})_{isoth}$  (Eq.2) for isothermal data of DPVC (solid symbols). Continuous lines are from linear regressions. Dotted line shows the slope=1. (b) Plot of  $S_C^{DYN}$  (Eq.3) versus  $\Delta(S_{exc})_{isoth}$  (Eq.2) for isothermal data of PPGE (open symbols). Continuous lines are from linear regressions. Dotted line shows the slope=1.

Fig.4 Logarithm of relaxation time as a function of the inverse of the product between temperature and “corrected” excess entropy,  $(TS_{exc}^C)^{-1}$  from Eq.(4b). From left to right: black close symbols are isobaric data of PPGE (the same as in Fig.2(b)) and coloured close symbols are isothermal data of DPVC (the same as in Fig.1(b)). Lines are from linear regressions.

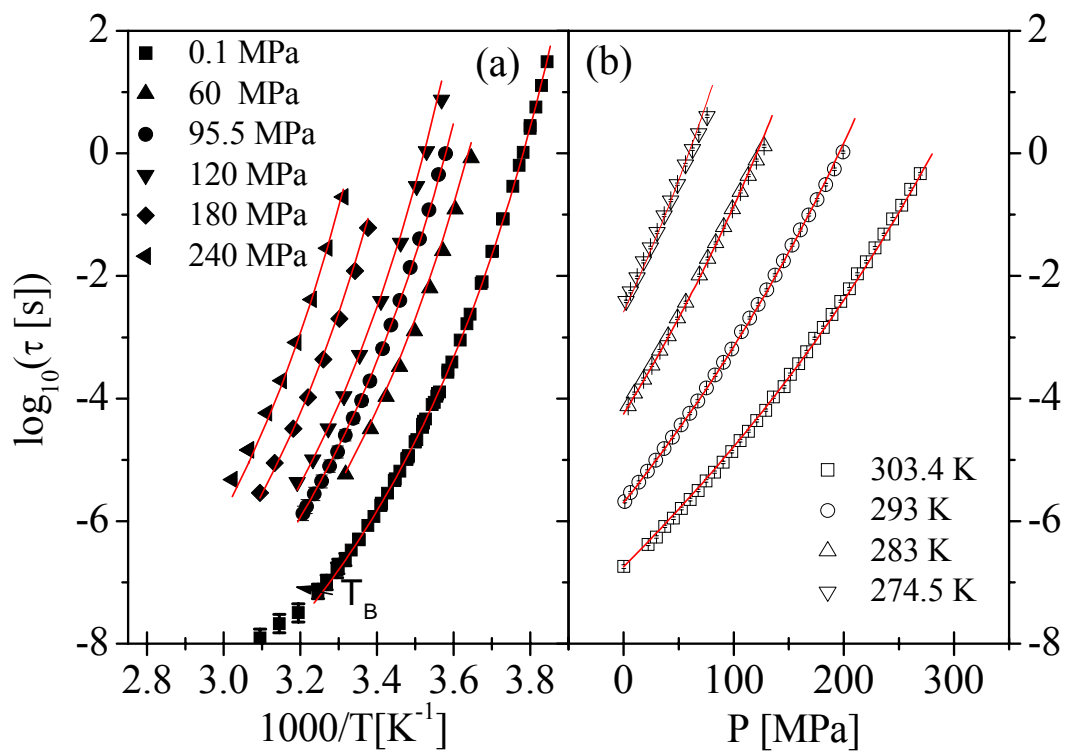
Fig.5 Logarithm of relaxation time (symbols) as a function of the inverse of the product between temperature and excess entropy,  $(TS_{exc})^{-1}$ . Solid symbols correspond to data at different isobaric conditions (indicated). The lines are fitting curves obtained with a least squares procedure. Inset: activation energy  $C_{AG}/g_T(P_{atm})$  (stars) plotted versus pressure, dashed line is from a linear regression.

Fig.6 Pressure derivative of the glass transition temperature plotted versus the quantity  $X$  of Eq.6. Star symbols indicate the systems studied in this paper. Circles are from literature data: glycerol (GLY) [45], propanol (n-PROH) [12, 46, 47], selenium (Se) [42], polyisoprene (1,4PiS) [48],  $B_2O_3$  [39, 42, 36], salol (SAL) [12, 49], polyvinylacetate (PVAc) [48, 38, 42], polyisobutene (PiBUTE) [48, 42], OTP and TCPM [12, 30, 50, 51, 52, 42], PDE and KDE [53, 54], polystyrene [48]. Additional values for pressure derivatives of  $T_g$  are from ref. [55]. Dashed, continuous and dotted lines are the predictions for  $g_T(P_{atm})/g_P(T)=0.6, 0.7, 0.8$  respectively.

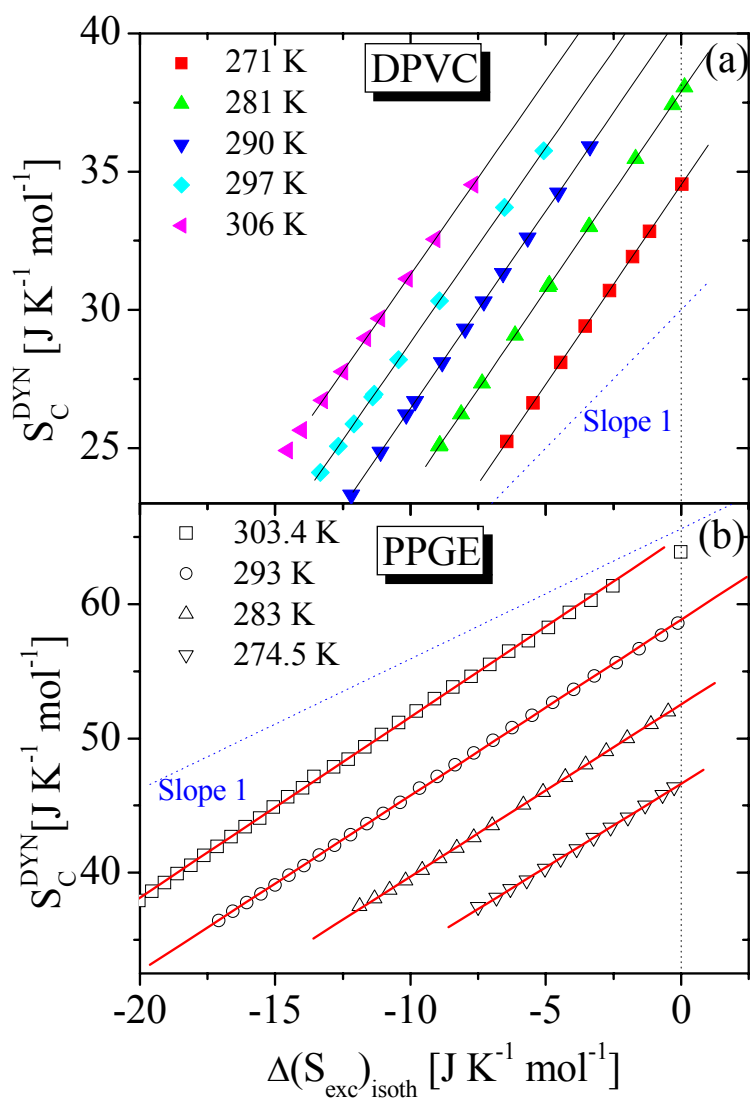


**Fig.1**



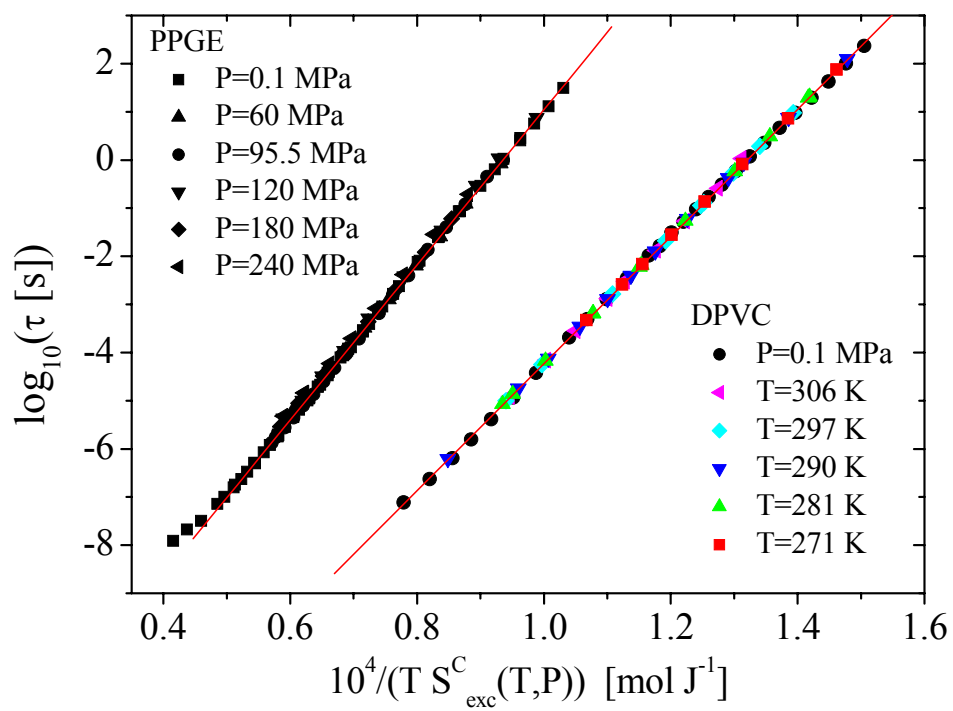


**Fig. 2**

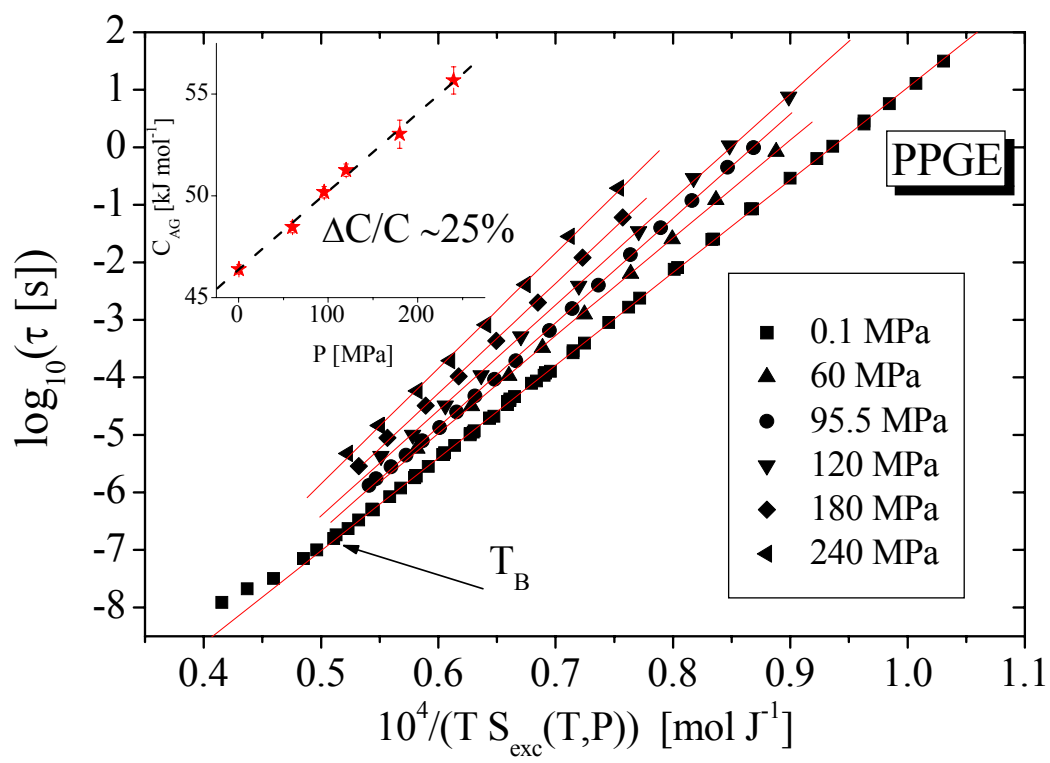


**Fig. 3**

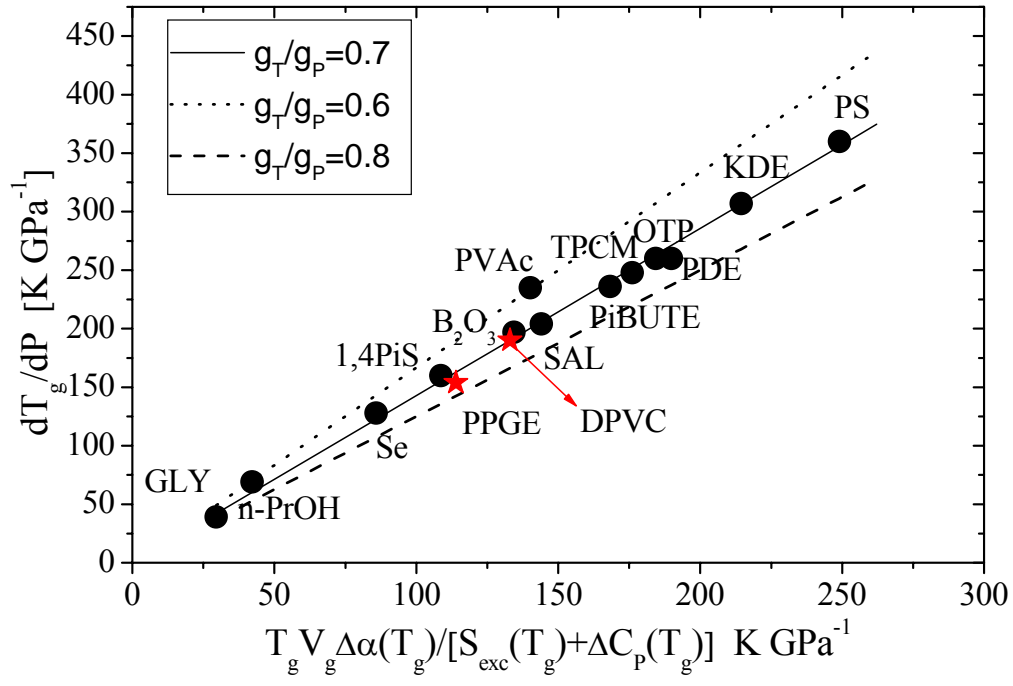




**Fig. 4**



**Fig. 5**



**Fig. 6**