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## Thermodynamical properties of glass forming systems: A Nuclear Magnetic Resonance analysis

Francesco Mallamace<sup>a,b,\*</sup>, Caterina Branca<sup>a</sup>, Carmelo Corsaro<sup>a</sup>, Jeroen Spooren<sup>a</sup>, Sow-Hsin Chen<sup>b</sup>, H. Eugene Stanley<sup>c</sup>

<sup>a</sup> Dipartimento di Fisica and CNISM, Università di Messina and IRCCS Neurolesi "Bonino-Pulejo" I-98166, Messina, Italy

<sup>b</sup> Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA

<sup>c</sup> Center for Polymer Studies and Department of Physics, Boston University, Boston, MA 02215, USA

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### ABSTRACT

We present a Nuclear Magnetic Resonance (NMR) study of the thermal evolution of the magnetic properties of three different glass formers: glycerol, o-terphenyl and salol. In particular, we analyze how the response of these liquids to the applied magnetic field changes with temperature. We focus on the total magnetization and on the chemical shift of each protonated group. By means of these quantities we account that the dynamics of the glass forming materials, on decreasing the temperature, is dominated by the onset of well defined local inhomogeneities due to precise microscopic cooperative processes. Just these "dynamical heterogeneities" and their energetic topology determine the dynamic crossover from fragile (super Arrhenius) to strong (pure Arrhenius) glass forming behavior. The specific heat changes evaluatable from the measured NMR chemical shift associate this phenomenon, and all the related ones, to local configurational changes.

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### 1. Introduction

Dynamical arrest (jamming) represents today one phenomenon that crosses many areas of knowledge. Its material facet is represented by glass transition, attained by decreasing temperature or increasing the system density, that, on despite the many efforts based on the more sophisticated theoretical model and experimental techniques of the modern statistical physics, is far from being completely clarified [1,2]. Supercooled liquids, i.e., liquids cooled below their melting point ( $T_M$ ), are considered the test systems to understand the basic mechanism of this transition to non-ergodic states.

In principle all liquids may be supercooled; in some cases crystallization takes place in the proximity of  $T_M$ , in other cases the physical evolution of a liquid is still observable on further cooling, and the liquid eventually solidifies directly into the glass phase. In such a situation all the dynamical properties of the material can be detailed as it goes to the arrest as a frozen liquid. Common observations, by decreasing  $T$ , are the onset of the  $\alpha$ -relaxation in the time dependent density correlation function (customary measured by means of scattering and dielectric relaxation techniques) characterized by the hierarchical multi-exponential temporal decay (the well-known stretched exponential form  $F(q, t) = F_q^c \exp[-(t/\tau)^B]$  [3]), and a re-

markable slowing down of more than 13 orders of magnitude in the dynamical parameters like the viscosity  $\eta$ , the average relaxation time  $\tau_\alpha$  and the self diffusion coefficient  $D_s$ . Such a dramatic change in the system properties is generally described by a non Arrhenius (or super Arrhenius, SA) behavior; i.e., on cooling these dynamical quantities increase faster than predicted by the well-known Arrhenius equation,  $\ln \eta / \eta_0 = E(T) / k_B T$ , where  $E(T)$  is an activation energy that increases significantly on cooling.

The clarification of the underlying microscopic origin of this slowing down represents a topic of much current research; a common opinion is that the manner in which the dynamical quantities approach their limiting values can provide proper details about the nature of the arrest phenomenon. The observation that, as  $T$  decreases to a fraction of  $T_M$ , transport coefficients increase to several orders of magnitude, surpassing in many cases the time required for experimental accessibility, has considered for a long time the onset of a "diverging behavior": a phase transition to a state in which the dynamical quantities become infinite following analogous laws of universality and scaling of critical phenomena. Although in the presence of conflicting opinions on the consistence of this approach in terms of a "criticality" in the system properties [3–8], many theoretical models, molecular dynamic simulations and a lot of refined experiments have been conducted to understand dynamical arrest. Even if these extensive studies have proposed many new ideas and possible interpretations of the arrest, essentially only one mathematical form has been used in the years to treat the dynamical

\* Corresponding author. Tel.: +1 39 090 6765016.

E-mail address: [francesco.mallamace@unime.it](mailto:francesco.mallamace@unime.it) (F. Mallamace).

data of the SA glass forming materials: the Vogel–Fulcher–Tammann (VFT) equation:

$$\eta = \eta_0 \exp\left(\frac{BT_0}{T-T_0}\right), \quad (1)$$

that, on the contrary to the Arrhenius one, predicts a well precise diverging behavior at a non-zero temperature  $T_0$ . The quality of the data fitting together with the diverging scales (of  $\tau(T)$ ,  $D_s(T)$  and  $\eta(T)$ ) contained within that equation has been considered essential ingredients to interpret the arrest process in terms of an underlying phase transition to a state of infinite relaxation time [9].

This idea, beside the fact that the experimental data are usually well fitted by the VFT, has been, over recent years, reasonably supported by the association of VFT fitting parameter  $T_0$  with the Kauzmann temperature [7]  $T_K$ , more precisely  $T_0 \sim T_K$ . The Kauzmann temperature  $T_K$  is an ideal glass temperature defined as the temperature where the configurational entropy,  $S_C$ , of the liquid phase extrapolated below the glass transition becomes identical to the crystal phase entropy. Such a situation comes easily out by considering the Adam–Gibbs theory [9] which relates the  $T$ -dependence of the structural relaxation time,  $\tau_\alpha$ , to the change in the  $S_C$  as:  $\tau_\alpha = \tau_0 \exp(C/TS_C)$ ; if  $S_C$  goes to zero at a finite temperature [e.g.,  $S_C = a(T - T_K)/T$ ], then one obtains the VFT form with the identification of the Kauzmann temperature with  $T_0$ . Indeed, this latter observation on the identity between  $T_K$  and  $T_0$  constitutes the basic support of the physical validity of Eq. (1).

A large class of experiments has also used the VFT formalism to relate  $T_0$  to the calorimetric glass transition temperature  $T_g$ , being  $T_M > T_g > T_K \sim T_0$ . In particular, a sort of classification for the glass forming liquids has been given by means of the concept of “fragility” [10]: “fragile” liquids have a marked VFT temperature dependence whereas “strong” ones exhibit a pure Arrhenius dynamical behavior. We must mention that it is commonly accepted that, whereas the Arrhenius behavior of supercooled liquids is theoretically interpreted in terms of single-particle hopping over potential barriers of uniform height, the super Arrhenius behavior has instead a cooperative character with a broad distribution of barrier heights. A good example of this collective behavior is represented by the thermodynamic description of supercooled systems in terms of so called inherent structures [11]. This approach is based on information of the potential energy topology, such as the number and depth of local minima (basins) of the potential energy landscape. In this framework, the short-time dynamics of the supercooled liquid has been associated with the intrabasin motion and the long-time slow dynamics with the interbasin one.

Another functional form used to study the temperature behavior of the super Arrhenius glass forming liquids dynamics is the power law:

$$\eta = \eta_0 \left[ \frac{T - T_x}{T_x} \right]^{-\theta}. \quad (2)$$

Also in this case the viscosity and the other transport parameters  $D_s(T)$  and  $\tau(T)$ , diverge at a certain temperature  $T_x$ . Such a power law approach comes out from some investigations of the dynamics of glass forming liquids which include explicitly the cooperative nature of their transport processes on a microscopic scale [12,13].

Starting from these considerations a study on the viscosity of a series of supercooled fluids, which range from very difficult to vitrify (e.g., pure bulk water) to excellent glass formers, shows that over a broad  $T$ -range their viscosities scale according to the above scaling form with  $1.5 < \theta < 2$  [14]. Besides this, Eq. (2) describes the  $T$ -dependence of the viscosity of a surprising variety of fluid systems in the high- $T$  regime (the SA region) better than the other forms commonly used to parametrize the  $\eta(T)$  data. The relevant observation in this viscosity study [14] is that  $T_x$  does not signal a sharp transition and does not coincide with  $T_g$  but it appears to be a significant temperature which marks the boundary between two types of viscous behavior. More precisely,  $T_x$  (where  $T_g < T_x < T_M$ )

represents a crossover temperature from fragile-to-strong (FS) glass former behavior. The liquid viscous behavior is Arrhenius for  $T < T_x$  whereas for  $T > T_x$  it is super Arrhenius and is well fitted by Eq. (2). The existence of a FS crossover at  $T_x \sim 228$  K has been successively considered for water [15] (just in view of water thermodynamical anomalies such as the isothermal compressibility  $K_T$ ) by assuming that its occurrence corresponds to a change in the liquid structure.

Roughly speaking, this latter experimental result suggests that supercooled liquids, on decreasing temperature, change progressively their dynamics from a sort of diverging behavior characterizing the high- $T$  regime to an Arrhenius one on approaching the arrest. In terms of the inherent structure picture, it seems that the temperature decrease is accompanied by an evolution of the supercooled liquid dynamics from one dominated by the intrabasin motions to another one in which the particles can move from one basin to another. In addition, the  $T$ -decrease determines a change in the basin number and configuration, i.e., a growth in their characteristic length scales and in their temporal stability.

The idea that, due to precise microscopic cooperative processes, upon cooling, a liquid does not become a glass in a spatially homogeneous fashion but becomes more and more highly spatially correlated, has recently received a growing body of evidence [8,16–21]. In the deeply supercooled region, by decreasing temperature, within the liquid originates spatial regions in which the structural relaxation time can differ by orders of magnitude from the average over the entire system; according to this description, the physics of the arrested process is dominated by the so called ‘spatially heterogeneous dynamics’ [18]. The presence of these heterogeneities has been argued to give rise to the breakdown of the Stokes–Einstein, SE, relation (or the appearance of the fractional Stokes–Einstein) and to the dynamic FS crossover [16,17,22,23] in a region located inside the supercooled phase at some temperature in the interval from  $T_g$  to  $T_M$ . Since the derivation of the SE relation assumes uncorrelated motion of particles, it is reasonable that the onset of correlations could result in a failure of the same relation. On these bases, the SE violation represents a useful element to study deeper aspects of the glass transition and other relevant phenomena observed in the interval  $T_M - T_g$ . A recent example is the study of the SE violation by means of the mode coupling theory (MCT) approach incorporating activated hopping processes [24].

Recent experiments [25–27] and molecular dynamic simulations [28–30] studies made in bulk and confined supercooled water confirm that the fractional SE is accompanied by a dynamic FS crossover, at the same temperature  $T_x \sim 225$  K. The existence of a temperature  $T_x$ , marking dynamical changes of fragile supercooled liquids below  $T_M$ , has been already considered in the past [5,14,31–36]. This interest is justified in view of strongly debated problems, like the existence of the dynamical divergence associated with the VFT form and the possibility that neither  $T_0$  nor  $T_g$  is relevant to describe and understand the slowing down in transport parameters of supercooled liquids.  $T_x$  like  $T_M$  is a quantity dependent on the material properties.

Very recently, by considering a glass forming system composed of particles interacting via soft potentials, it has been explicitly demonstrated by Eckmann and Procaccia that the configurational entropy is finite at any temperature [8], i.e., a Kauzmann temperature,  $T_K$ , where the liquid is out of the equilibrium, does not exist and thus the VFT may be considered only a fitting formula. A subsequent study [35] of the dielectric relaxation times  $\tau(T)$  fully confirms the suggestions that there is no compelling evidence for the VFT prediction that transport parameters diverge at a finite  $T$  and provides a demonstration, in terms of an Avramov form ( $\tau(T) = \tau_0 \exp(B/T^n)$ ), that the use of the VFT cannot represent a fruitful route to explain supercooled liquid dynamics. This analysis deals with  $\tau(T)$  of many ultraviscous glass forming fluids fitting the data in the equilibrium phase far from the dynamical arrest; the obtained results well agree with the main findings of Ref. [8], and are also confirmed by considering the segmental relaxation data of glass forming polymers as  $T - T_0$  approaches zero [37]: the time scales related

to the arrest may not diverge at finite temperature. Similar observations have been reported also for polymers and small molecule glass formers (see, e.g., references [7–9] of Ref. [37]) suggesting that the main finding of the model proposed for soft systems can have a larger generality.

A common theme of many works on glass forming liquids is that, inside the region of the supercooled phase limited by the crossover temperature  $T_x$ , their transport parameters such as viscosity [5,14,34] and dielectric relaxation times [32,35,36] can have universal features. For example by using for  $\eta$  a  $\tilde{T} = T_g/T$  representation [34] a master curve only for  $T < \tilde{T}$  is obtained, whereas for  $T > \tilde{T}$  deviations occur and, at highest  $T$ , data were fitted by using the VFT formula. In addition, the analysis of the relaxation times and the viscosities (of 58 liquids) in terms of the parabolic form  $((T_o/T) - 1)^2$  exhibit a certain degree of universality inside the interval  $T_x < T < T_o$  [36]. In that case  $T_o$  is defined as an onset temperature where the liquid dynamics crosses over from that of a simple liquid to that of a strongly correlated material like a glass former;  $T_o$ , as  $T_x$ , depends on the material.

The conclusions of Refs [35,36], the theoretical indication [8] together with the finding of cited works invoking the existence of a crossover temperature [5,14–36], propose that the VFT approach must be reconsidered for the explanation of the dynamical arrest. Motivated by these latter studies and considering the results obtained in water, we have recently examined the temperature behavior of the viscosity and other transport coefficients of many liquids [38]. In particular, on considering a very large number of different materials (84), by using Eq. (2), we have demonstrated that the dynamical FS crossover represents a general property of glass forming liquids. However, in that work we have given also a proof (independent from any model) that the FS crossover, the appearance of the fractional Stokes–Einstein and the dynamical heterogeneities are directly linked with  $T_x$ . This was made in terms of a very simple scaling approach by plotting  $D_s$  vs.  $\eta$  in a log–log scale; we have observed that all the plotted data of different supercooled fluids collapse in a single master curve that clearly shows two different scaling behaviors above and below the fragile-to-strong crossover temperature  $T_x$ . It must be noted that for all the liquids the onset of the breakdown takes place at  $\eta_x \approx 10^3$  Poise.

Also the measured fractional exponent  $\zeta = 0.85 \pm 0.02$  highlights the correspondence at  $T_x$  among the dynamical FS crossover, the fractional Stokes–Einstein and the dynamical heterogeneities. The measured  $\zeta$  value ( $\zeta = 0.85 \pm 0.02$ ) agrees with the finding of other experimental [17,27] and theoretical studies predicting the presence of a crossover from hierarchical super Arrhenius dynamics for short length scales to pure Arrhenius at larger ones [6,23]. Moreover, this value coincides with that obtained by the extended MCT approach for which the crossover is caused by the change in the dynamics from the one determined by the cage effect to that dominated by hopping processes [39].

These considerations represent the basis of the actual work aimed, by considering three “prototypes” of glass forming materials like glycerol, salol and o-terphenyl (OTP), to demonstrate that  $T_x$  signals the locus of a genuine change in the physics behavior of supercooled liquids. A situation that is well described by means of the relevant quantities measured in a Nuclear Magnetic Resonance (NMR) experiment directly from the  $^1H$  NMR spectra (obtained by the free induction decay or FID). In particular, we evaluate the temperature dependence of the system equilibrium magnetization intensity  $M_0(T)$  (or the susceptibility  $\chi(T)$ ) and of the chemical shift  $\delta(T)$ . We show that  $T_x$  is closely related to a peak in the configurational specific heat at constant pressure extracted by means of a novel approach directly from  $\delta(T)$  [40]. This is in agreement with the Adam–Gibbs theory [9] which relates the  $T$ -dependence of the structural relaxation to the change in the configurational entropy of the system  $S_C(T)$ .

## 2. Experimental section

In general, relaxations measured in an NMR experiment are caused by random fluctuations of the magnetic field at the position of a resonating

spin originating by the thermal motion of neighboring spins. The NMR signal intensity is directly related with the system equilibrium magnetization,  $M_0(T)$  (or the magnetic susceptibility  $\chi$ ) which depends linearly on the total number of mobile spins per unit volume, on the mean square value of nuclear magnetic moment and on  $1/T$  (Curie law). The chemical shift  $\delta$  is an assumed linear response of the electronic structure of a system under investigation to an external magnetic field  $B_0$ , as  $B(j) = (1 - \delta_j)B_0$ , where  $j$  is an index identifying the chemical environment [41,42]. Specifically,  $\delta$  is related to the magnetic shielding tensor  $\sigma$ , which in turn relates to the local field experienced by the magnetic moment of the observed nucleus. The magnetic shielding tensor  $\sigma$ , strongly dependent on the local electronic environment, is a useful probe of the local geometry (an example is the hydrogen bond structure for water and aqueous systems and solutions [43]). Of interest are the isotropic part,  $\sigma_{iso} \equiv \text{Tr}(\sigma/3)$ , and the shielding anisotropy  $\Delta\sigma \equiv \sigma_{33} - (\sigma_{11} + \sigma_{22})/2$ , where  $\sigma_{11}$ ,  $\sigma_{22}$ , and  $\sigma_{33}$  are the three principal components of  $\sigma$ .  $\sigma_{iso}$  is experimentally obtained via the measured proton chemical shift relative to a reference state through the relation [44]

$$\delta = \sigma_{iso}^{ref} - \sigma_{iso} + \left(A - \frac{1}{3}\right) (\chi^{ref} - \chi). \quad (3)$$

Here  $\chi$  is the magnetic susceptibility, and the factor  $A$  depends on the sample shape and orientation:  $A = 1/3$  for a spherical sample. Since the magnetic field exerted on a proton is  $B_0[1 + (4\pi/3)\chi(T)]$ , the resonance frequency is  $\omega(T) = \gamma H_0[1 - \sigma(T) + (4\pi/3)\chi(T)]$ , where  $\gamma$  is the proton gyromagnetic ratio. Thus, the deviation of  $\sigma(T)$  from a reference value gives  $\delta(T)$ .

The chemical shift  $\delta(T)$  depends on the number and the species of next neighbor molecules to the probe nucleus being proportional to the average number of local configurations  $\langle N_C \rangle$ . Hence, according to the entropy definition  $S_C \approx -k_B \ln \langle N_C \rangle$ . Therefore the temperature derivative of the measured chemical shift,

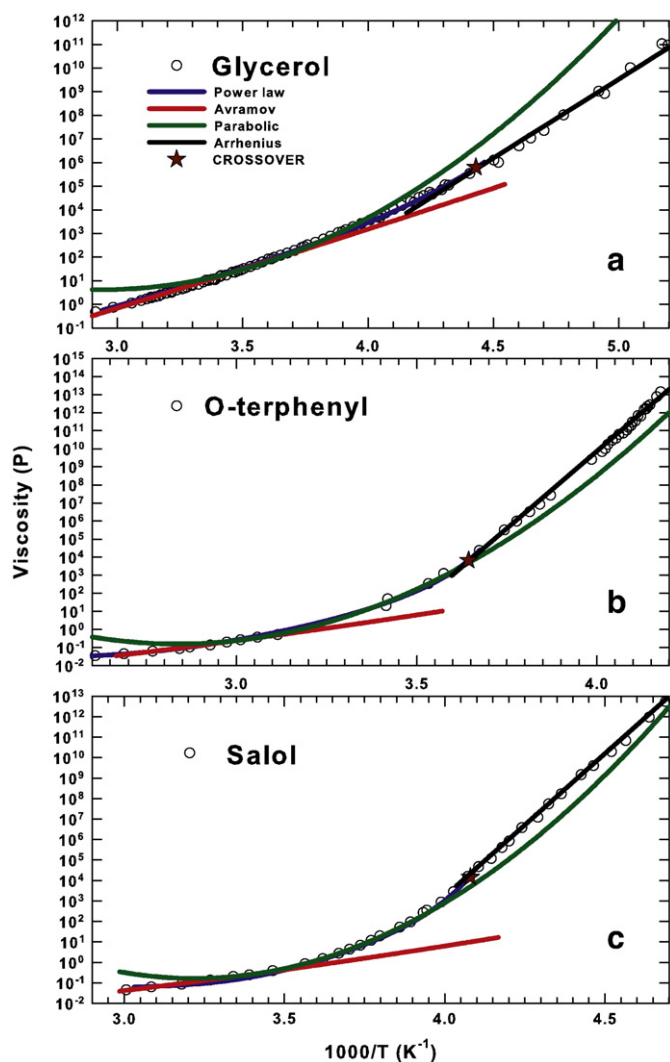
$$-\left(\frac{\partial \ln \delta(T)}{\partial T}\right)_p \approx -\left(\frac{\partial \ln \langle N_C \rangle}{\partial T}\right)_p \approx \left(\frac{\partial S_C}{\partial T}\right)_p, \quad (4)$$

should be proportional to the constant pressure configurational specific heat  $C_{p,c}(T)$  (being  $C_p = T(\partial S/\partial T)_p$ ).

Dynamical properties of glycerol, salol and OTP, were studied at ambient pressure and different temperatures by using a Bruker AVANCE NMR spectrometer, operating at 700 MHz  $^1H$  resonance frequency. In these NMR experiments we have measured the chemical shift and the equilibrium magnetization  $M_0$  of the  $^1H$ NMR spectra (obtained by the free induction decay (FID)). The explored temperature ranges are different for the three different systems but we cover, with an accuracy of  $\pm 0.2$  K, a range that goes from the stable liquid phase  $T > T_M$  to temperatures below the calorimetric  $T_g$ . In particular, for glycerol (with  $T_M \sim 292$  K and  $T_g \sim 190$  K) we have studied the range  $170 < T < 320$  K; for salol ( $T_M \sim 318$  K and  $T_g \sim 220$  K) the studied  $T$ -range is  $205 - 330$  K and finally for o-terphenyl ( $T_M \sim 328$  K and  $T_g \sim 246$  K) we worked in the range  $230 - 340$  K. The  $T$ -dependence of the chemical shift of methanol was used as a  $T$  standard. Samples were studied by cooling or heating procedures obtaining the same spectra. High purity samples were obtained from Aldrich. Glycerol (99.5%,  $< 0.1$  water content) was transferred under nitrogen flow into the NMR cell without further drying or purification, whereas OTP ( $> 99\%$ ) and salol ( $> 99\%$ ) were purified according to well established procedures [31–33].

## 3. Results and discussion

Before discussing the findings of our experiment, we consider, as reported in Fig. 1, the viscosity of the three studied supercooled liquids (Fig. 1a–Glycerol [45], Fig. 1b–OTP [46] and Fig. 1c–Salol [46]). The  $\eta(T)$  data are reported in an Arrhenius plot ( $\log \eta$  vs.  $1000/T$ ). As it can be seen a crossover from a fragile-to-strong glass forming behavior is evident in



**Fig. 1.** The shear viscosity  $\eta$ , of glycerol (a), o-terphenyl (b) and salol (c) which presents a dynamical crossover from super Arrhenius to Arrhenius behavior. The data are analyzed for  $T > T_x$  by means of the three main approaches recently proposed (power law [14], Avramov [35] and parabolic [36]); for  $T < T_x$  data are fitted by an Arrhenius form. For all samples the power law well fits the data in all the interval  $T > T_x$  better than the other forms that work only in opposite regions of that interval (the Avramov works for the highest  $T$ , and the parabolic holds only for the lowest).

all the plots where the crossover temperature ( $T_x$ ) is indicated by a star. The measured  $T_x$  are located for the three materials in the supercooled liquid phase and are  $T_x^{GLY} = 225 \pm 5$  K,  $T_x^{OTP} = 274 \pm 5$  K and  $T_x^{SAL} = 245 \pm 5$  K for glycerol, OTP and salol respectively. In all figures the data fitting by using three different functional forms are also reported: the Avramov (red curve), the parabolic (green curve) and the power law represented by Eq. (2) (blue curve). Among the three fitting procedures, the power law is the only one that well reproduces the data points in all the SA region predicting also, for the reasons given above, the region in which falls the crossover temperature. The other forms work well only in a limited  $T$ -range: the Avramov only at the highest  $T$  and the parabolic in a finite range for  $T > T_x$ . According to the recent results concerning the non-diverging nature of supercooled materials, we have considered just these materials that are unambiguously characterized by a dynamical crossover without reporting a data fitting by means of the VFT relation.

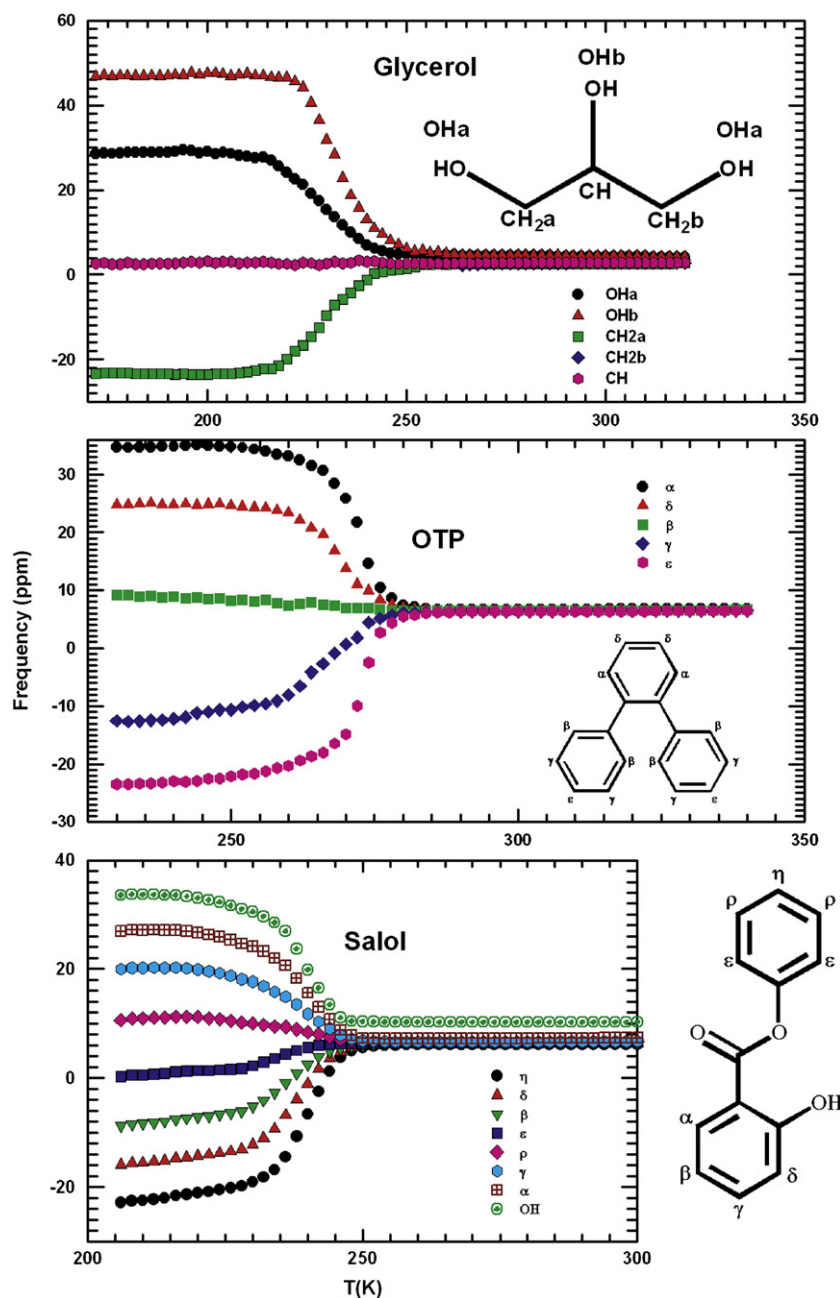
Now, just to show as an NMR experiment well reproduces on molecular basis the dynamical FS crossover, we consider, Fig. 2, the proton chemical shift frequencies  $\delta(T)$  of the protonated groups of the three studied materials, Fig. 2a-Glycerol, Fig. 2b-OTP and Fig. 2c-Salol. In each figure, the sample chemical structure is reported with the

indication of the studied functional groups that are precisely the following: i) glycerol ( $C_3H_5(OH)_3$ ) possesses three hydroxilic groups, two external (OHa) and one central (OHb), besides the central CH and the two external methylenes  $CH_2a$  and  $CH_2b$ ; ii) OTP ( $C_{18}H_{14}$ ) has some aromatic CH groups, namely  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\epsilon$ , disposed in three rings; iii) salol ( $C_{13}H_{10}O_3$ ) possesses one hydroxyl (OH) and different aromatic (CH) groups,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\rho$ ,  $\epsilon$  and  $\eta$ , disposed in two rings.

As it can be seen from Fig. 2, for all the samples the supercooled region is characterized by three main temperature intervals: a) the higher  $T$ -region, including also  $T_M$ , in which the chemical shift changes are minimal; b) the intermediate  $T$ -range in which the  $\delta(T)$  of some groups changes simultaneously and dramatically at a very deep supercooled temperature (e.g., for salol, Fig. 2c, such a temperature is about 70K below the corresponding  $T_M$ ) and c) the lowest  $T$ -region where the dynamics remains stable. The changes observed in  $\delta(T)$  regard mainly the OH and the external molecular groups (for some groups  $\delta(T)$  increases and for the remaining there is an equivalent decrease) indicating a growth in the intermolecular correlation. Roughly speaking, the local shielding changes originating a sort of molecular clustering driven by the strong decrease in the molecular mobility (see the  $\eta(T)$  behavior on decreasing  $T$ , Fig. 1). Internal groups appear to be less sensitive to temperature variations. As previously said, such a change in the system chemical shift  $\delta(T)$  implies a change in the configurational entropy  $S_C$ , and then in the configurational specific heat  $C_{p,c}(T)$  that may be evaluated by a temperature derivative of the measured  $\delta(T)$  according to Eq. (4). The obtained results for the configurational specific heat  $C_{p,c}(T)$  of the three supercooled liquids are reported in Fig. 3, Glycerol (Fig. 3a), OTP (Fig. 3b) and Salol (Fig. 3c). In all the samples a maximum in  $C_{p,c}(T)$  is evident at a temperature that corresponds, within the experimental errors, to the value at which the system shear viscosity evidences the dynamical FS crossover ( $T_x$ ). More precisely, we obtain:  $T_{MCP}^{GLY} \approx 229$  K,  $T_{MCP}^{OTP} \approx 271$  K and  $T_{MCP}^{SAL} \approx 238$  K. Practically, this observation gives evidence that the dynamical FS crossover is accompanied by a change in the system local structure and dynamics.

A proof of this result is given by the magnetization,  $M_0(T)$ , measured for the three samples as a function of the temperature in the same intervals in which the proton chemical shift has been studied.  $M_0(T)$  is a quantity directly proportional to the magnetic susceptibility  $\chi$  ( $\chi = M_0/H$ , where  $H$  is the magnetic field) that, at the thermal equilibrium, according to the classical magnetism, is sensitive to the average angle between the direction of the atomic magnetic moment  $\mu$  and the applied field  $H$ . According to the well-known Curie law, it is related to the mean square value, per unit volume, of the nuclear magnetic moment reflecting hence the local structural properties of the system (see e.g., [44]). The measured values of  $M_0(T)$  are reported in Fig. 4 (also in this case the same order adopted before for the studied liquids is held). For each sample we have reported some characteristic temperatures, i.e., the melting ( $T_M$ ), the glass transition ( $T_g$ ), the FS crossover ( $T_x$ ) measured by means of the viscosity and the NMR configurational specific heat maximum  $C_{p,c}$ . Besides, we have reported some temperatures characterizing significant changes in other physical quantities such as the average relaxation times obtained by means of the dielectric relaxation and light and neutron scattering.

A first observation is that in all the systems, Glycerol (Fig. 4a), OTP (Fig. 4b) and Salol (Fig. 4c), above the melting temperature,  $M_0(T)$  is nearly constant according to the Curie law. Approaching the deeply supercooled phase (well inside the SA region)  $M_0(T)$  evidences in all systems a sharp decrease followed by a slower one. The FS crossover is located inside the temperature interval of the sharp decrease at about the flex point of the system magnetization. Looking at the Glycerol case (Fig. 4a) we have to stress that the relative maximum at  $\approx 270$  K may be associated with a liquid–liquid transition (a sort of  $\lambda$ -transition) as detected by NMR [47] and dielectric relaxation [48]. In the same figure we also report the values of the ideal MCT temperature ( $T_{0,Glyc}^{MCT} \sim 225$  K) as measured by means of neutron and light scattering [49] and that of the rotational relaxation time crossover ( $T_{rot} \sim 229$  K) obtained by using



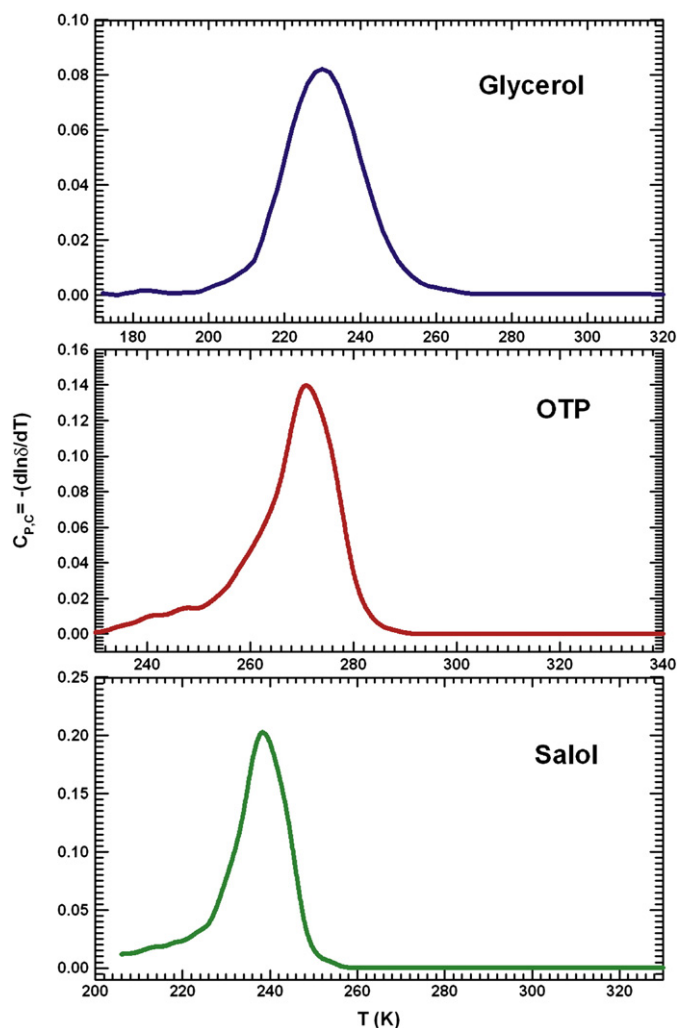
**Fig. 2.** The proton chemical shift frequencies  $\delta(T)$  of the protonated groups of the three studied materials: Glycerol (a), OTP (b) and Salol (c). In each panel, the sample chemical structure is reported and the studied functional groups are the following: i) glycerol ( $C_3H_8(OH)_3$ ) the three hydroxyl groups, two external (OHa) and one central (OHb), besides the central CH and the two external methylenes CH<sub>2</sub>a and CH<sub>2</sub>b; ii) OTP ( $C_{18}H_{14}$ ) has some aromatic CH groups, namely  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ , and  $\epsilon$ , disposed in three rings; iii) salol ( $C_{13}H_{10}O_3$ ) possesses one hydroxyl (OH) and different aromatic (CH) groups,  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\rho$ ,  $\epsilon$  and  $\eta$ , disposed in two rings.

the depolarized light scattering in the gigahertz regime [50]. An analogous situation can be observed also in the OTP case (Fig. 4b). Here, all the crossover temperatures observed from  $\eta(T)$ , the NMR self diffusion coefficient  $D_s(T)$  [51] and the  $C_{p,c}(T)$  fall in a very narrow temperature range ( $275 \pm 5$  K). Also the ideal MCT temperature ( $T_{0,OTP}^{MCT} \sim 280$  K) measured by the use of different experimental techniques [52,53] falls in this interval. For such a system the maximum in the calorimetric specific heat was measured at about 260 K [46]. Finally, we consider the salol case (Fig. 4c) where the temperatures characterizing different physical quantities are distributed inside the magnetization sharp decrease in a more spread way if compared with the other two cases. The maximum of the  $C_{p,c}(T)$  is located at  $\sim 238$  K, in good agreement with the maximum observed in the calorimetric specific heat at  $\sim 230$  K [46], whereas the dynamical FS crossover

temperature, obtained from  $\eta(T)$  [46] and  $D_s(T)$  [17] data, is at  $T_x \sim 245$  K. Furthermore, the temperature of the onset of the non-ergodicity parameter observed in the density–density correlation function ( $T \sim 265$  K), as measured by the impulsive stimulated light scattering technique [33] is about  $10^\circ$  higher than the ideal MCT crossover temperature obtained by Raman and Brillouin light scattering ( $T_{0,Sal}^{MCT} \sim 256$  K) [31].

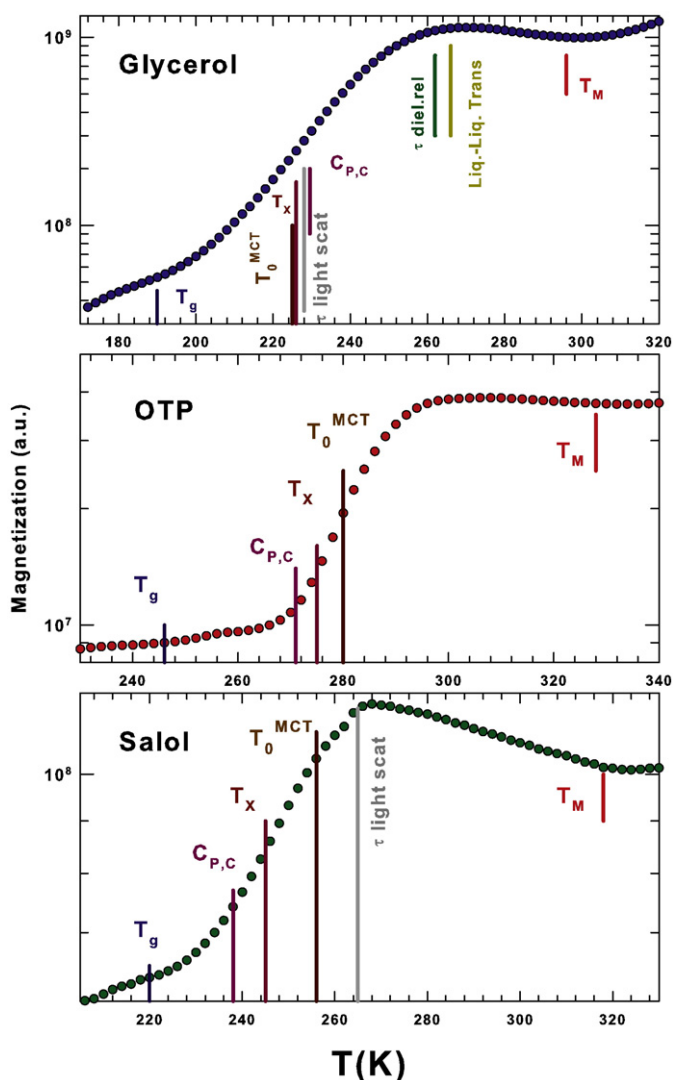
#### 4. Conclusions

Taking into consideration the recent results obtained in super-cooled liquids from which there is evidence that the VFT law is not a fruitful tool in describing their SA behavior, we have considered the hypothesis that all of these systems are characterized by a dynamical



**Fig. 3.** The configurational specific heat  $C_{p,c}(T)$  of the three supercooled liquids: Glycerol (a), OTP (b) and Salol (c). The maxima in  $C_{p,c}(T)$ ,  $T_{MCP}^{GLY} \approx 229$  K,  $T_{MCP}^{OTP} \approx 271$  K and  $T_{MCP}^{SAL} \approx 238$  K, correspond, within the experimental errors, to the value at which the system shear viscosity evidences the dynamical FS crossover ( $T_x$ ), see e.g. Fig. 1.

crossover from fragile to strong glass forming behavior. The actual idea is that such a process is due to the fact that a liquid, upon cooling, does not become a glass in a spatially homogeneous fashion but there is the onset of more and more highly spatial correlated regions originated by microscopic cooperative processes. This behaves the growth of long living structures (a sort of clustering) with a different energetic topology that dominates the SA region. So that in this regime the system dynamics is dominated by multi-relaxation processes whereas the very supercooled phase can be easily described by a simple Arrhenius behavior. Hence, if the SA dynamics is regulated by collective intercluster processes (mediated by the cluster size and kinetics) the Arrhenius behavior is only due to the hopping over potential barriers of uniform height. In other words there is in supercooled liquids a crossover from an average intracuster motion (the SA phase) to an intercluster long-time slow dynamics. On these bases we have considered the idea that the equilibrium magnetization (easily measurable by means of the NMR FID) and the associated nuclear chemical shift can give proper details on these underlying heterogeneities and thus of the dynamical FS crossover and of the other phenomena connected to it. Since the NMR signal is very sensitive to the system structure and mobility, the variation with the temperature of both the magnetization and the chemical shift reflect the changes in the system mobility driven by the temperature effect. In fact, when the liquid is in its thermal stable phase (above the melting point), the magnetization is nearly  $T$ -independent according to the Curie law.



**Fig. 4.** The equilibrium magnetization,  $M_0(T)$  measured for the three samples. For Glycerol (a) the relative maximum at  $\approx 270$  K may be associated with a liquid–liquid transition as detected by NMR [47] and dielectric relaxation experiments [48]. The ideal MCT temperature ( $T_0^{MCT} \sim 225$  K) [49] and the rotational relaxation time crossover ( $\tau$ - light scat  $\sim 229$  K) [50], are also reported. An analogous situation can be observed also for OTP (b). Here, all the crossover temperatures observed from  $\eta(T)$ , the NMR self diffusion coefficient  $D_s(T)$  [51] and the  $C_{p,c}(T)$  fall in a very narrow temperature range ( $275 \pm 5$  K). Furthermore, also the ideal MCT temperature ( $T_0^{MCT,OTP} \sim 280$  K) measured by the use of different experimental techniques [52,53] falls in this interval. Finally, for salol (c) the maximum of the configurational specific heat is located at  $\sim 238$  K, in good agreement with the maximum observed in the calorimetric specific heat at  $\sim 230$  K [46], whereas the dynamical FS crossover temperature, obtained from  $\eta(T)$  [46] and  $D_s(T)$  [17] data, is at  $\sim 245$  K. Furthermore, the temperature of the onset of the non-ergodicity parameter, observed in the density–density correlation function ( $T \sim 265$  K) [33], is about  $10^\circ$  higher than the ideal MCT ( $T_0^{MCT,SAL} \sim 256$  K) [31].

Whereas, when the dynamics of the system is driven by association processes, the magnetization changes dramatically.

Therefore, we have conducted a Nuclear Magnetic Resonance study of the thermal evolution of the magnetic properties of three different glass formers: glycerol, o-terphenyl and salol. In particular, we have analyzed how the response of these liquids to the applied magnetic field changes with temperature. We have focused on the total magnetization  $M_0(T)$  and on the chemical shift of each protonated groups  $\delta(T)$  as a function of the temperature. In the first case we have demonstrated as such a quantity really highlights the system structural changes on the basis of the complex dynamical evolution of the glass forming material whereas in the second case, being able to evaluate the configurational specific heat, a quantity of relevant interest for the dynamical arrest, we unambiguously have proved that the dynamical FS crossover corresponds to a local

topological variation in the configurational degrees of freedom; as evidenced by the fact that  $C_{p,c}$  presents a maximum just at about the same temperature ( $T_x$ ) where transport parameters show the dynamical FS crossover (see Fig. 4).

In conclusion, we stress that it is non-trivial the approximate coincidence among the FS crossover temperature, the temperature of the maximum in the configurational specific heat and the idealized MCT temperature [39], measured for all three systems by means of different techniques. This naturally leads to a physical interpretation of the dynamical behavior of supercooled fluids as a crossing by a regime dominated by “clustering” to one dominated by “hopping” processes; i.e., paraphrasing the historical inherent basin approach: a transition from an intrabasin to an interbasin particle motions.

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