Can experiments select the configurational component of excess entropy?

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We introduce an experimental method of assessing the vibrational and configurational components of the excess entropy of a liquid over crystal, based on a joined investigation of dynamic and thermodynamic properties as a function of temperature and pressure. We analyze light scattering, dielectric, calorimetric and dilatometric measurements of three prototype glass formers, orthoterphenyl, salol, and glycerol. In all cases we find that about 70% of the excess entropy is configurational in nature.

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Liquids become glasses as a consequence of the suppression of long range molecular mobility. The most evident feature that accompanies glass formation is a dramatic increase of the structural relaxation time, τ_{α} . A key for understanding this phenomenon is the Adam-Gibbs (AG) theory [1], which states a relationship between τ_{α} and the configurational entropy S_c ,

$$\tau = \tau_0 \exp\left(\frac{C}{TS_c}\right). \tag{1}$$

Here, $S_c \equiv S^{melt} - S^{vibr}$ where S^{melt} is the entropy of the metastable liquid phase, and S^{vibr} is the entropy of an ideal amorphous-solid phase (ideal glass) in which only vibrations are active; C is nearly constant, and τ_0 is the relaxation time in the high temperature limit.

The difficult point in testing the predictions — and the validity itself — of Eq. (1) is the evaluation of the configurational entropy from experimental data. In the past, this problem has been overcome by approximating the vibrational heat capacity at low temperatures by the heat capacity of an experimentally accessible solid phase, i.e., the crystal or the glass [2]. Therefore, *configurational* entropy is replaced by *excess* entropy. Notwithstanding, the AG equation succeeds in describing experimental results. This fact looks like a paradox, since the same evidence is also found in computer simulation studies, where the actual configurational entropy is calculated. An approximate proportionality between configurational and total excess entropies could be a possible explanation of the paradox. From Eq. (1) it is evident that relaxation time measurements performed as a function of temperature alone, cannot help to distinguish between S_c and a quantity proportional to it, as the proportionality constant simply renormalizes the value of C.

Numerical simulations of supercooled water, and analytical models for thermodynamics of defect crystals (see Ref. [3]), seem to support this idea. On the other hand, to our knowledge, the only experimental work assessing the two separate contributions to excess entropy has been made on a very simple material, elemental selenium [4]. In this case, the vibrational entropy over crystal is calculated under harmonic approximation from the analysis of neutron-scattering data, and it is subtracted from S_{exc} to determine S_c . This result gave rise to controversial con-

clusions about the method of calculation of S_c , and the existence of proportionality between S_c and S_{exc} ([3, 5]).

Here, we enter the debate trying to answer the question: "Can experiments select the configurational component of excess entropy in glass forming systems?". We show that calorimetric, dilatometric, and relaxation measurements as a function of both temperature T and pressure P, allow us to extract the configurational fraction of the excess entropy. Our method is tested on three different prototype glass formers, orthoterphenyl, salol, and glycerol and for relaxation data, obtained by dielectric spectroscopy and light scattering.

The configurational entropy of a system at a given Tand P can be separated into an isobaric contribution at zero pressure, and an isothermal contribution at temperature T [6]:

$$S_{c}(T,P) = S_{c}^{isob}(T,0) + S_{c}^{isoth}(T,P) =$$
$$= \int_{T_{K}}^{T} \frac{\Delta C_{P}(T')}{T'} dT' - \int_{0}^{P} \Delta \left(\frac{\partial V}{\partial T}\right)_{P'} dP',$$
(2)

where $\Delta C_P = C_P^{melt} - C_P^{vibr}$ is the configurational heat capacity at zero pressure, $\Delta\,(\partial V/\partial T)_P = (\partial V/\partial T)_P^{melt} (\partial V/\partial T)_P^{vibr}$ is the configurational thermal expansivity at T, and T_K is the temperature where the configurational entropy of a liquid vanishes at P = 0. Substituting Eq. (2) in Eq. (1) gives the pressure extended AG equation (PEAG) [6]. For evaluation purposes, also in this approach one approximates the isobaric part of the configurational entropy with the excess entropy, i.e., $S_c^{isob}(T,0) \approx S_{exc}(T,0)$. Within this approximation, the PEAG model is able to describe experimental data fairly well in the T-P space [6, 7]. The cost to be payed is a value of $(\partial V/\partial T)_P^{vibr}$ which in some cases may considerably depart from the expected value. This anomaly is a consequence of the poor approximation $S_c \approx S_{exc}$. In contrast, in this work we improve the PEAG model, we obtain a reasonable value for $(\partial V/\partial T)_P^{vibr}$, and, more interestingly, we determine a realistic estimate of the configurational entropy.

The model.— Guided by the idea that an approximate proportionality may exist between configurational and



FIG. 1: a) Structural relaxation time of OTP from dielectric measurements at different pressures. Open symbols are data taken at different pressures [12] (P=0.1 MPa (\circ), 19.6 MPa (\triangleleft), 39.2 MPa (\triangle), 58.8 MPa (\diamond), 78.5 MPa (\Box)). Crosses are data at ambient pressure [13]. b) Structural relaxation time $\langle \tau \rangle$ of OTP from photon-correlation measurements at different pressures. Data taken from Fytas et al.[14] (P=0.1 MPa (\triangleleft), 25 MPa (\Box), 50 MPa (\circ), 75 MPa (\triangleright), 100 MPa (\star), 125 MPa (\oplus)). c) Structural relaxation time $\langle \tau \rangle$ of salol from photon correlation measurements at different temperatures [7] (T=267.0 K (\triangleright), 268.5 K (\circ), 271.1 K (\triangle), 274.5 K (\diamond), 278.2 K (\oplus), 280.4 K (\Box)). d) Structural relaxation time of glycerol from dielectric measurements at different temperatures (data taken from Ref. 19): T=217.5 K (\triangleleft), T=230.6 K (\diamond), T=240.9 K (\Box), T=247.3K (\circ). In all panels, the solid lines represent the best fit with the PEAG equation Eq. (4). The relaxation time for dielectric measurements is $\tau = 1/2\pi\nu_{max}$, with ν_{max} the frequency of maximum dielectric loss. The average relaxation time for photon correlation data is given by $\langle \tau \rangle = (\tau_K / \beta_K) \Gamma(\beta_K^{-1})$, where τ_K and β_K are the Kholrausch-Williams-Watts [20] characteristic time and stretching parameter, respectively, and Γ denotes the Euler gamma function.

excess entropies, we shall assume that the isobaric contribution to S_c can be expressed, to first approximation, as a fraction of the total excess entropy:

$$S_c(T,0) = \Phi S_{exc}^{isob}(T,0). \tag{3}$$

Hence, we modify the PEAG formula for the structural relaxation time as follows:

$$\tau(T,P) = \tau_0 \exp\left[\frac{C}{T(\Phi S_{exc}^{isob} + S_c^{isoth})}\right]; \qquad (4)$$

here, the parameter Φ (≤ 1) quantifies the fraction of excess entropy at atmospheric pressure configurational in nature. Note that the presence of the term S_c^{isoth} in Eq. (4) prevents the parameter Φ to play the role of a simple renormalization constant.

The liquid over crystal excess entropy at atmospheric pressure, $S_{exc}^{isob}(T,0)$, can be evaluated from calorimetric measurements. In calculating the isothermal part of

the configurational entropy, $S_c^{isoth}(T, P)$, we do not make any modification of the expression given in Ref. [6], since no mention to a reference state — crystal or glass — was necessary. Accordingly, we approximate the vibrational thermal expansivity at P by its value at ambient pressure, i.e., $(\partial V/\partial T)_P^{vibr} \approx (\partial V/\partial T)_0^{vibr}$ [Eq. (2)]. This is due to the fact that the value and the pressure dependence of the thermal expansivity for crystals and glasses is usually much smaller than that for liquids. Therefore, we are left with calculating the integral over pressure of the thermal expansivity of the melt. Starting from the Tait equation of state [8], simple algebra allows us to express this contribution in terms of thermodynamic parameters obtained from dilatometric measurements [6].

Testing the model.— A complete test of the model requires the use of information determined by several experimental techniques, i.e, T and P-dependence

structural relaxation times, extended calorimetric data, pressure-volume-temperature (PVT) measurements. In the following we consider three model glass-formers: orthoterphenyl (OTP), phenyl salycilate (salol), and glycerol. For these systems all the needed data are available, and can be properly used to test the generality of our approach. Altogether, calorimetric, volumetric and $\tau(T,0)$ data provide all the parameters in Eq. (4) — for details see Ref. [6] — except for C, Φ and $\left(\frac{\partial V}{\partial T}\right)_0^{vibr}$, which can be obtained by a multi-variable fit on experimental relaxation data as a function of T and P.

Orthoterphenyl.— Isobaric heat capacity of crystalline, supercooled and stable liquid OTP determined via calorimetry [9] has been used to calculate the liquid over crystal excess entropy S_{exc} as a function of temperature. Specific volume data of the liquid and glassy OTP as a function of both temperature and pressure [11] have been used to determine the parameters of the Tait equation of state. Structural relaxation times obtained by means of two different techniques are available from the literature. A study of pressure effects on the dielectric relaxation of supercooled OTP [12] reports several isobaric measurements as a function of temperature which are shown in Fig. 1a together with dielectric data at ambient pressure [13]. A second pressure and temperature dependent photon correlation investigation has been reported in [14]. The average relaxation time $\langle \tau \rangle$ appears in Fig. 1b in the T and P ranges investigated.

We fit according to Eq. (4) the data in the T range 247-272 K at atmospheric pressure, where $\log_{10} \tau$ is linear vs. $(TS_{exc})^{-1}$), and all the isobaric dielectric data at higher pressures. The simultaneous fit gives: $\Phi = 0.69 \pm 0.05$, $(\partial V/\partial T)_0^{vibr} = (4.3 \pm 0.7) \times 10^{-8} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1}$, C = $(1.49 \pm 0.12) \times 10^5$ J mol⁻¹. It is evident from Fig. 1a the high quality of the agreement between experimental relaxation time data for OTP (symbols) and calculated curves (solid lines) using the PEAG model in the form of Eq. (4). As a cross-check of the reliability of the fit performed on the dielectric relaxation data, we plot the same curves as in Fig. 1b on the PCS data. We find that the PCS data are perfectly described by the same fitting parameters as the dielectric data, except for a vertical shift corresponding to a different value of τ_0 connected with the specific technique used. It is worth stressing that the best-fit is set by a physical value of the vibrational thermal expansivity: the obtained value compares well with $\sim 5 \times 10^{-8} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1}$, that is expected for an OTP-based solid form of matter [11]. Reasonably, the value of the vibrational thermal expansivity corresponds to about 30% of the melt thermal expansivity. We remark that using the PEAG form with a preset $\Phi = 1$ we find an unphysical value for the vibrational thermal expansivity $(2.3 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1})$, about two order of magnitude lower than the expansivity of the melt.

Salol.— Precise determination of the heat capacity of salol under atmospheric pressure is due to Oguni [15]. Dilatometric measurements V(T, P) of crystalline and liquid salol have recently been carried out [16] permit-



FIG. 2: Entropy components in OTP at atmospheric pressure. Circles represent the excess entropy of the liquid over the crystal, $S_{exc} = S^{melt} - S^{crystal}$, calculated from experimental calorimetric data. The best fit with $S_{exc}(T) = S_{\infty} - k/T$ for T>247 K, and its extrapolation for T<247 K are shown with solid and dash line, respectively. The thick dash-dot line represents the configurational entropy evaluated as a fraction of the excess entropy, $S_c = \Phi S_{exc}$. T_K =203.8 K is the temperature at which the entropy of the liquid equals the entropy of the crystal.

ting to extract the parameters of the Tait equation of state. Isothermal relaxation times measured by photoncorrelation spectroscopy are available [7]. The pressure variation of $\langle \tau \rangle$ is shown in Fig. 1c in the temperature range investigated. We analyze the relaxation times data using Eq. (4), and find $\Phi = 0.68 \pm 0.08$, $(\partial V/\partial T)_0^{vibr} = (3.8\pm0.7)\times10^{-8} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1}$, and $C = (1.9\pm0.3)\times10^5$ J mol⁻¹. The value for the vibrational thermal expansivity is in remarkable agreement with that found for the poly-crystal via PVT measurements $[(\partial V/\partial T)_0^{crystal} \sim (4.0\pm0.5)\times10^{-8} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1}]$ [16]. A previous analysis of these data performed by some of us [7] using a preset $\Phi = 1$, i.e. replacing S_c with S_{exc} , provided $(\partial V/\partial T)_0^{vibr} = (1.0\pm0.7)\times10^{-8} \text{ m}^3 \text{ mol}^{-1} \text{ K}^{-1}$, which is in feeble agreement with the experimental value of the poly-crystal.

Glycerol.— Isobaric heat capacity of liquid-glass and crystal glycerol [17] have been used to evaluate the liquid over crystal excess entropy. Volumetric measurements of glycerol reported in Ref. [18] as a function of both T and P have been represented in terms of the Tait equation. As far as $\tau(T, P)$ data, we focus on the pioneering work by Johari and Whalley [19], which provides relaxation time data in agreement with those recently reported by Lunkenheimer at atmospheric pressure [21]. For our test, we subject to the fit procedure data up to ~ 1 GPa (see Fig. 1d) excluding all isotherms at temperature higher than 247 K, in order to remain in the validity range of the PEAG model. Because of the not very high quality of the data, and with the background of the analysis of OTP and salol in place, we undertake the fit procedure with $(\partial V/\partial T)_0^{vibr}$ constrained to a physical value. Dilatometric measurements of glycerol provide an average value $(1.68 \pm 0.01) \times 10^{-8}$ for the thermal expansivity of the glassy state in the temperature range investigated. As a result of a global fit procedure we find $C = (12.8 \pm 0.4) \times 10^5$ J mol⁻¹, and $\Phi = 0.71 \pm 0.01$ [22], this value being surprisingly close to that found in OTP and salol.

In summary, the fundamental information we gain from the above analysis is that at atmospheric pressure, about 70% of the excess entropy is of configurational origin for each one of the molecular systems here considered. These results astonishingly agree with the value found for S_c/S_{exc} (0.69) in selenium [3], where the configurational entropy was calculated from neutron scattering data. In addition, we observe that simulation studies on SPC-E water [23, 24, 25] have shown S_c and S_{exc} to be proportional, with a constant ratio of about 0.77 [3].

In conclusion, we have introduced a general method to

calculate the configurational contribution to the excess entropy for molecular liquids. The general validity of the method and the reasonableness of the hypothesis made are tested on three model glass formers. The results obtained include the following points: *i*) Experiments performed as a function of T and P are actually able to identify the configurational fraction of excess entropy, giving a positive answer to our initial question; *ii*) The value of the configurational fraction of excess entropy reconciles the results obtained by previous laboratory and computational tests; *iii*) Configurational entropy is confirmed to be a key concept in controlling the slow dynamics of glass forming systems.

This last evidence is also confirmed by the energy landscape approach to the glass transition [26], as highlighted by recent simulation studies (see, among others, Refs. [23, 27, 28, 29, 30, 31]). We believe that more efforts should be devoted in order to clarify the connection among the potential energy landscape features (see, for instance, the equation of state proposed in Refs. [31, 32]) and experimental results in T and P domains.

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