An entropy based theory for the viscosity of strong glasses

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One of the main applications of the stochastic matrix method is the evaluation of the probability of finding boroxol rings and dendrites in a boron oxide glass. In this work, we calculate the configurational entropy of B_2O_3 using this probability and Shannon's definition of entropy. The isentropic temperature is evaluated obtaining a very good agreement with experimental data. Entropy is introduced into the Adam-Gibbs equation to calculate viscosity. The resulting expression fits the complete range of temperatures for the supercooled liquid.

Keywords: Supercooled liquid; glass transition; viscosity; entropy.

Una de las principales aplicaciones del método de las matrices estocásticas es la evaluación de la probabilidad de encontrar anillos de boroxol y dentritas en un vidrio de óxido de boro. En este trabajo se calcula la entropía del B_2O_3 utilizando esta probabilidad y la definición de entropía de Shannon. se evalúa la temperatura isentrópica obteniendo un muy buen acuerdo con los datos experimentales. La entropía se introduce en la ecuación de Adam-Gibbs para calcular la viscosidad. La expresión obtenida se ajusta a los valores reportados en le intervalo completo de temperaturas para el líquido sobreenfriado.

Descriptores: Líquido sobreenfriado; transición vítrea; entropía.

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1. Introduction

In the last two decades, a large amount of both theoretical and experimental studies have been undertaken in order to describe the relaxation processes and transport properties in glass forming liquids. Two of the most significant features in these systems are the abrupt increase in viscosity as the glass transition temperature T_g is approached, and the slowing down of structural relaxation. Different kinds of glass forming liquids have been classified according to the behavior of viscosity with temperature in terms of the so-called fragility [1–6]. Strong glass formers, mainly metallic glasses, such as B_2O_3, follow an Arrhenius type equation,

$$\log \eta = -A + \frac{B}{T} \tag{1}$$

while intermediate and fragile liquids are best described by the Vogel-Fulcher-Tammann equation,

$$\log \eta = -A_{VFT} + \frac{B_{VFT}}{T - T_0} \tag{2}$$

It is important to point out that in Eqs. (1) and (2) A, B, A_{VFT}, and B_{VFT}, are adjustable parameters for a given fit of experimental data.

Both Eqs. (1) and (2) describe the viscosity of the supercooled liquid in the region where very slow diffusional processes occur. These processes have been defined as α-relaxation processes. In the past decade, experiments have indicated the existence of fast relaxation processes in the vicinity of T_g [7–12], referred to as β-relaxation processes, through evidence of drastic changes in the transport properties of the glass forming liquid, especially the diffusion mechanisms [13–17], around a cross-over temperature T_c which lies in the range between 1.15 T_g and 1.28 T_g [18–20]. Thus, claims exist asserting that empirical equations such as the ARR and VFT equations are not adequate to fit the experimental data for viscosity in the complete temperature interval from T_g toT_m, the melting point temperature.

In order to analyze the validity of different empirical forms for the experimental data of the viscosity in several glass forming liquids, Stickel *et al.* [21, 22] introduced the temperature derivatives method, which has been widely used to study the behavior of different kinds of glasses [23–28]. Their results indicate that different empirical forms are needed to fit data in the different temperature intervals that appear through the onset of a crossover of two regimes in the neighborhood of T_c. In the specific case of the strong-glass former boron oxide (B_2O_3), where T_g is approximately

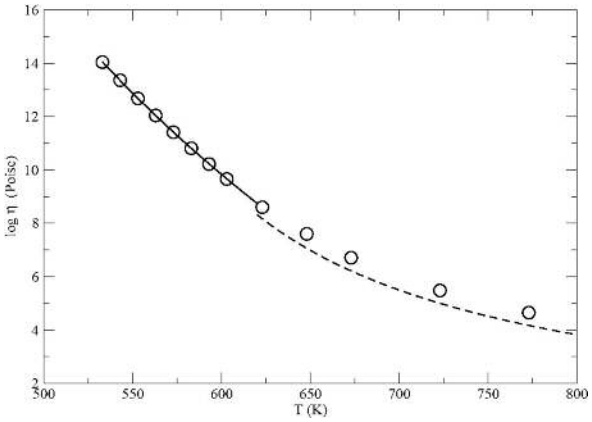

FIGURE 1. Experimental data for the viscosity of B_2O_3 (o) [29], and the Arrhenius (solid line) and Vogel-Fulcher-Tammann (dashed line) proposed by Stickel *et al.* [22].

530 K and T_m = 720 K, early studies for the viscosity showed that it was not possible to fit a unique empirical form for the viscosity in the supercooled system [29]. Stickel *et al.* predict that two different equations must be used to reproduce the experimental data for viscosity in the supercooled liquid: an Arrhenius type equation between 533 K and 620 K, and a Vogel-Fulcher-Tamann type from 620 K up to the melting point, as can be seen in Fig. 1.

The main trend of thought offered in this work is based on the fact that one of the most successful theoretical efforts to deal with the description of structural relaxation processes in supercooled liquids was developed by Adam and Gibbs [30] in terms of the configurational entropy S_c of the system. Their main result is that either the viscosity or, equivalently, the structural relaxation time is related to S_c through the equation,

$$\log \eta = \frac{C}{2.303 T S_c(T)} \tag{3}$$

where C is a constant related to the activation energy, given by

$$C = \frac{\Delta\mu s_c^*}{k_B}$$

where $\Delta\mu$ is largely the potential energy hindering the cooperative rearrangement, s_c^* is the critical configurational entropy [30] and S_c(T) is the configurational entropy. This entropy plays a fundamental role, for its specific functional form in different supercooled liquids determines the temperature dependence of the viscosity. Several works have been presented in the literature to find different forms for the configurational entropy in glass formers [31–34].

In this work, we present an expression for the temperature dependence of viscosity of B_2O_3 that describes its behavior in range from 533 K to the melting point, using a theoretical model which allows the calculation of configurational entropy for the glass former. There are two issues in this argumentation that require a careful analysis. The first one concerns the physical nature of the Adam-Gibbs theory, which relies heavily on the concept of configurational entropy, and the second one concerns the concept of configurational entropy itself. We may recall that, in the Adam-Gibbs theory, the underlying structural relaxation time increases as configurational entropy decreases, as Eq. (3) indicates. However some authors [25] argue that this fact is in contradiction with experimental findings, claiming that the critical number of molecular units, denoted by $z*$ in this theory, is usually too small to be accommodated in pores larger than a certain size [35, 36]. This may be true in the case of liquids composed of large molecules, such as ethylene glycol, salol, and others, but Adam-Gibbs appears to work for strong glass formers as pointed out in Ref. 37. Here, however, we are not dealing with the specific nature of the constant C appearing in Eq. (3), but as argued below, it will be taken to be simply an adjustable parameter not necessarily implying accommodation of molecular units, although indeed related to S_c. As for configurational entropy, a word of caution is in order. It happens that not all authors in this field accept a unique concept behind this quantity. In this paper, the configurational entropy will be taken in its most orthodox interpretation, namely, the contribution of the entropy arising from the number of ways in which the molecules composing the glass forming liquid can be accommodated in a given lattice-like structure [38]. It is this interpretation of S_c which will allow us to use the method outlined in Sec. 2. Wheter the outcome of this calculation agrees or not with other possible interpretations is a matter for future debate.

To present our results, in Sec. 2 we calculate the configurational entropy of B_2O_3, in Sec. 3 we evaluate its viscosity, and finally in section 4 we present a discussion of our work.

2. Configurational entropy for B_2O_3

In this section we present the calculation of the configurational entropy for B_2O_3, as defined in the previous section, using Shannon's definition for entropy and the stochastic matrix method to evaluate the probability of forming either a boroxol ring [26,27] or a dendrite [37] in the system.

In recent theoretical works, the stochastic matrix method (SMM) has been used by Kerner [39] to describe the growth process of a solid and by Barrio *et al.* [40] to derive the fraction of boroxol rings in a boron oxide glass. The underlying idea of this method consists in modeling the growth of a solid considering two main ingredients: border and bulk. The border (or rim) is composed of all those entities that offer a potential possibility for a new unit to adhere and agglomerate. The bulk consists of all units that have saturated all their bonds. The growth process at the rim is then represented by a matrix whose components are the probabilities of finding a given site at the rim of a cluster of units of a certain size. The matrix acts on a vector whose components represent the probabilities of finding a given site on the rim of a cluster. The matrix acting on a vector transforms it into a new one, since the rim has changed by adding a new atom (or unit). Further, the probability factors include two contributions, the statisti-

cal weight for each process and a Boltzmann factor, taking into account the energy barrier required to form a bond. By successive application of the matrix to the resulting vectors, one finds the final configuration characterized by the eigenvector of the matrix whose eigenvalue is one which is assumed to exist and is unique. Once the selected eigenvector has been obtained, one can find the probability of forming a ring from one layer to another. For the specific case of B_2O_3, such probability P_a is given by

$$P_a = \frac{24\xi^2 + 16\xi}{84\xi^2 + 107\xi + 25} \tag{4}$$

where ξ = exp $(E_2 - E_1)/k_BT$ [26]. E_1 and E_2 are the characteristic energies related to the formation of a single B-O-B unit and a boroxol ring respectively, and $E_2 - E_1$ = -4.927 cal mol^{-1}[40]. Recently, the SMM has been used to describe the relaxation processes in B_2O_3 [26,27]. We may also describe the case in which, instead of rings, the links correspond to the formation of dendrites by means of the probability P_d [37].

The formation of these two possible structures should be a consequence of the way in which the supercooled B_2O_3 evolves towards glass. Hence, the final configuration of the system is exclusively determined by both types of local structures. Thus, configurational entropy may be directly evaluated from these configurational changes and it will depend only on the probabilities of forming either rings or dendrites. On this basis, using Shannon's definition of entropy [41], we may write the configurational entropy for our system, namely,

$$S_c = S_{ca} + S_{cd} = -k_B(P_a \ln P_a + P_d \ln P_d) \tag{5}$$

with P_d the probability observing a dendrite in the system, $P_d = 1 - P_a$. In Fig. 2 we exhibit the configurational entropy in terms of the temperature. In addition, in the insert of this figure, we present the relative contributions of S_{ca} and S_{cd}. As it is easily seen, the main contribution comes from the ring formation, which is about 80%. The difference between both entropies grows as the glass transition temperature is approached. This result is in good agreement with experimental observations with Raman spectroscopy that suggest that the glass transition in B_2O_3 takes place at the temperature where the breakdown of the boroxol rings occurs [42]. It is important to remark that, even though Raman intensity data for molten B_2O_3 near T_g show a rapid breakdown of boroxol rings, around 20 % of the contribution to configurational entropy comes from the dendrites and cannot be ignored.

Substituting the probabilities of finding a ring or a dendrite into Eq. (5), the explicit value for configurational entropy is obtained, namely

$$S_c = -k_B \left\{ \frac{24\xi^2 + 16\xi}{84\xi^2 + 107\xi + 25} ln \frac{24\xi^2 + 16\xi}{84\xi^2 + 107\xi + 25} + \frac{60\xi^2 + 91\xi + 25}{84\xi^2 + 107\xi + 25} ln \frac{60\xi^2 + 91\xi + 25}{84\xi^2 + 107\xi + 25} \right\} \tag{6}$$

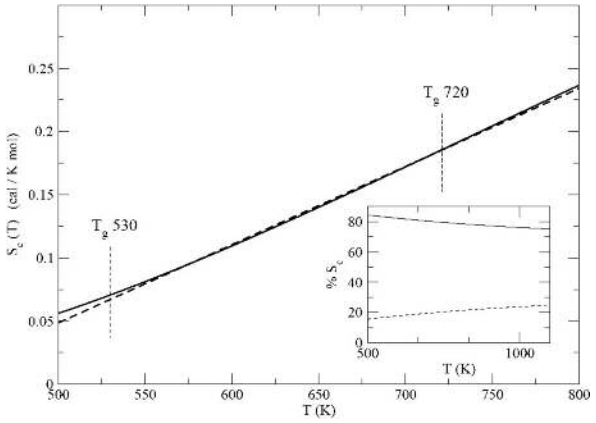

FIGURE 2. Plot of the configurational entropy given by Eq. (6) (solid line), with $E_2 - E_1$ = -4.927 kcal mol^{-1} [37], and the straight line fit (dashed line) represented by Eq. (7), with m = 6.19092 $\times$ 10^4 kcal /mol K^2, b = - 0.261067 kcal/mol K. In the insert we exhibit the percentage of the contributions of rings (solid line) and dendrites (dashed line) to the total configurational entropy, Eq. (5).

This configurational entropy may be interpreted as follows: As the temperature changes, even though the positions of the atoms of the system are not affected, the probability of any atom to form either rings or dendrites does change. As it was explained in Ref. 37, the reason to include the probability of dendrite formation in the system is that not all bonds in a strong glass former necessarily lead to the formation of rings.

As we mentioned before, in Fig. 2 we depict the configurational entropy given by Eq. (6) with the solid line. This complicated form for the dependence of S_c with temperature may be almost perfectly (deviation=0.99) fitted to a straight line (dashed line) in the region of the supercooled liquid, given by

$$S_c(T) = mT + b \tag{7}$$

where

$$m = 6.19092 \times 10^{-4} \text{cal/mol } K^2$$

and

$$b = -0.261067 \text{cal/mol} K.$$

Thus, instead of using the expression for S_c given by Eq. (6), which is a rather complicated function of ξ, use will be made of Eq. (7) to compute the viscosity through Eq. (3) in the temperature range 530<T<720. We can observe the existence of an isoentropic temperature T_0, in the way proposed by many authors [32,34,43,44], namely, $S_c(T_0)$ = 0 whose value is 416.7 K, that finally depends on the energy difference E_2-E_1. The existence of T_0 has been one of the main aspects that appear in the studies of the configurational entropy in the glass transition. It is important to point out that our value for T_0 lies within a 3.25% error when compared to the value reported by Angell and Rao [45] for T_0, namely T_0 = 402 K, on a strictly empirical basis.

3. The viscosity

In spite of the comments given in the introduction, the Adam Gibbs theory has proved to be a very useful tool for the interpretation and discussion of transport and relaxation processes in glass forming liquids, both strong and fragile, and a large number of studies have been performed to test its validity. Recent literature shows that this theoretical approach is still influencing many researchers in the field of the glass transition [32,34,36,46-49]. As we discussed before, some authors like Ngai [36,50] refer to some inadequacies of this theory, especially when the constant C in Eq. (3) is interpreted in terms the size of the cooperatively rearranging regions, as well as in experiments in nanometric scales and the determination of configurational entropy, mainly from calorimetric results [33]. As we have already mentioned, we believe that in our case these shortcomings could be relevant in complex glass forming liquids, but at least for strong liquids, previous results seem to be immune to these problems. We will assume that this is the case, and we shall use Eq. (3) in its generic form, that means, ignoring the dependence of C on $z*$.

We may now obtain an explicit expression for the viscosity of B_2O_3 introducing the configurational entropy given by Eq. (7) into the Adam-Gibbs form, namely Eq. (3). Thus we find that

$$\log \frac{\eta}{\eta_0} = \frac{K}{aT^2 + T} \tag{8}$$

where η_0 is a reference viscosity, such that $\log \eta_0$ = 2.5419, $a = m/b$ and K = $(2.303)^{-1} C b^{-1}$. The Adam-Gibbs constant C is adjusted as the parameter that best fits experimental data for viscosity, which in our case turns out to be C = 1043.65 cal/mol . Using the relation

$$\frac{S_c^*}{S_c(T_g)} = \frac{T_0}{T_g - T_0}$$

obtained elsewhere [51], we find that for B_2O_3, s_c^* = 0.271 cal/ K mol, a value that is comparable with those of other glass formers [51]. Moreover, the square temperature dependence for the viscosity observed in Eq. (8) has been reported for other systems in the literature [52,53]. In Fig. 3 we display a plot of the viscosity predicted by Eq. (8) and the experimental data [29] for B_2O_3 reproduced in Table I. It is seen that the agreement of our equation with the experimental values for viscosity in the temperature range from T_g to T_m is satisfactory.

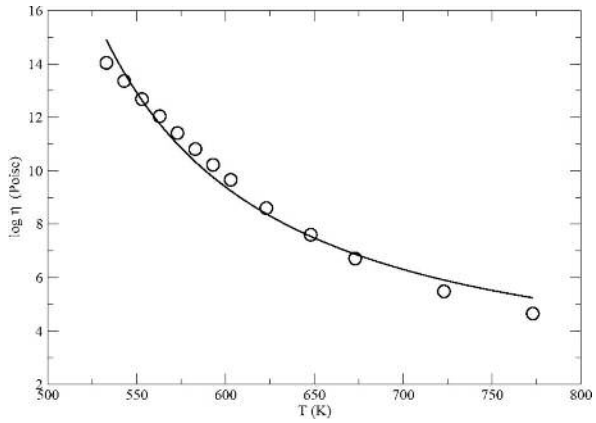

FIGURE 3. Theoretical prediction for log η , Eq. (8), and the corresponding experimental data (o)[29].

TABLE I. Experimental data for log η reported by Macedo and Napolitano [29].

Temperature (K)	Log η (η / Poise)
533	14.04
543	13.36
553	12.68
563	12.04
573	11.41
583	10.81
593	10.22
603	9.66
623	8.60
648	7.60
673	6.71
723	5.48

4. Discussion

The Adam-Gibbs equation proves to be a suitable relation between the viscosity of a supercooled strong glass forming liquid and its configurational entropy as obtained from Eq. (3). In this work , we have presented an example of this relationship for the case of a strong glass former, namely B_2O_3, through the evaluation of the probabilities of the system to form either rings or dendrites. It would be straightforward to apply this method to chalcogenide glasses such as As_2Se_3. Contrary to previous statements, this form for S_c enables us to obtain an expression for the viscosity of the system that fits the whole temperature range from the glass transition temperature to the melting point. We predict a very good value for the isentropic temperature without any adjustable parameters, using only the experimental value for $E_2 - -E_1$. The method outlined here, namely the stochastic matrix method, seems to work well for strong liquids, but its validity in intermediate and fragile liquids may be questionable because the fragile glasses are formed by very long chains.

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