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# Thermodynamic properties of borate glasses by molecular dynamics simulations

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**Abstract.** The molecular dynamics method was used to examine the  $B_2O_3$  and borate glasses. The discontinuity in each of the thermodynamic factors such as the transition temperature, specific heat, thermal expansion and thermal compressibility is detected and checked by the so-called Prigogine–Defay ratio and it is found that this ratio exceeds unity for the systems studied. This behaviour indicates that multiple order parameters are required to characterize the glassy state. Also it is found that the formation of diborate groups in borate glasses reduces the value of the Prigogine–Defay ratio  $\Pi$ , while the formation of groups with non-bridging oxygen ions increases the value of  $\Pi$ , i.e. increases the number of order parameters.

## 1. Introduction

Molecular dynamics (MD) simulations have been a very useful tool in investigating the structure and properties of glasses in the past few years. MD calculations yield detailed information about the thermodynamic properties of glass. The transition from the liquid to glass states is an attractive subject from the thermodynamic point of view.

Studies on the structure of boron oxide, borate and borosilicate glasses have been reviewed extensively by many workers. Zachariassen [1] in 1932 introduced a three-dimensional network model for the triangular  $BO_3$  in boron oxide glasses. Since then, many models have been presented to explain the behaviour of glasses containing different ratios of alkali oxides. The changes in some physical properties such as specific heat and thermal expansion at a specific concentration of alkali oxide have been discussed in the light of the boron anomaly.

A discontinuity in each of the thermodynamic properties during cooling of the glass melt was observed by Kauzmann [2] and by Davies and Jones [3]. They attributed this discontinuity to changes in the structure in which glass is trapped in a single configuration state below a specific temperature, namely the glass transition temperature  $T_g$ , while the liquid above  $T_g$  has the opportunity to exist in more than one state depending on the liquid temperature and the observation time.

For a thermal equilibrium system of  $N$  particles at a temperature  $T$  and pressure  $P$ , Jackle [4] derived some relationships describing the discontinuity in each of the thermodynamic properties as:

$$\lim_{T \rightarrow 0} [(1/V) \overline{(\Delta H)^2}] = k_B T_g^2 \Delta C_p(T_g) \quad (1)$$

$$\lim_{T \rightarrow 0} [(1/V) \overline{\Delta H \Delta V}] = k_B T_g^2 \Delta \alpha(T_g) \quad (2)$$

$$\lim_{T \rightarrow 0} [(1/V) \overline{(\Delta V)^2}] = k_B T_g \Delta K_T(T_g) \quad (3)$$

where  $\Delta H$  and  $\Delta V$  are the changes in the enthalpy and volume, respectively, and  $\Delta C_p$ ,  $\Delta \alpha$  and  $\Delta K_T$  are the excesses in the specific heat, thermal expansion and coefficient of compressibility at the glass transition temperature. Also,  $k_B$  has its usual meaning of the Boltzmann constant. Whereas these relations are very useful to describe the behaviour of glass at  $T_g$ , the Prigogine–Defay [5] ratio

$$\Pi = [\Delta C_p(T_g) \Delta K_T(T_g)] / T_g [\Delta \alpha(T_g)] \quad (4)$$

is more generalized to express the fluctuation in the thermodynamic properties at the glass temperature in terms of a single order parameter or multiple order parameters. The order parameters might represent the number of holes or vacancies in the liquid, or the number of broken or flexed bonds of various types. Also, in glass, they might represent the number of sites with particular coordination geometry or the number of specific groups such as diborate, metaborate, triborate, etc.

Experimental determinations of the Prigogine–Defay ratio  $\Pi$  have been made for a number of glasses by Gupta and Moynihan [6] and by Moynihan *et al* [7]. The glassy state is characterized by fixed values of a set of structural ordering parameters such as the microscopic domains or the discrete chains, rings and sheets. Bray and co-workers [8–10] found by NMR studies that groups such as triborate, pentaborate and diborate are the skeleton of the structure of glass.

The main task of this work is to correlate the values of the Prigogine–Defay ratio obtained by the computer simulations with the values obtained experimentally and the relation between these values and the structure of glasses.

## 2. Experimental details

### 2.1. Simulation method

In the computer experiment, a combination of the isobaric MD method due to Andersen [11] and the isothermal method due to Nosé [12] was used. The advantage of this method is to produce an  $(N, P, T)$  ensemble whereas the commonly used MD method is to produce an  $(N, V, E)$  ensemble. The classical equation of motion with constraints for the atoms distributed randomly, according to the Maxwell distribution, in a cubic box with an edge depends on the experimental density of the system and was numerically integrated to yield a time record of the position and velocity coordinates of the atoms. Our calculations were performed using a double-precision VAX/VMS computer. The interactions of pairs of atoms within a sphere of radius 4.0 Å were considered. In some cases the cut-off radius was increased to 5.5 Å. Spheres of large radii did not add more accuracy to the results.

The pair potential for ion–ion interaction was calculated using the Born–Mayer–Huggins (BMH) formula:

$$V_{ij} = A_{ij} \exp(-r/\rho) + (Z_i Z_j e^2 / r) \operatorname{erfc}(r/\eta) \quad (5)$$

where  $A_{ij} = (1 + Z_i/n_i + Z_i/n_j)b \exp[(r_i + r_j)/\rho]$  and the other BMH parameters used in this work are given in [13]. The numerical integration routine due to Verlet [14] with a time increment of  $10^{-15}$  s was used. Although the chosen potential is purely ionic, it is found that the calculated ionic force shows agreement with a large amount of experimental data. To overcome the divergence of the long-range Coulomb interaction, an expression based on the Ewald sum and modified by Soules [15] was used in the MD calculations.

## 2.2. Temperature scaling

At the beginning the atoms for each species, shown in table 1, were given a random Maxwell distribution corresponding to a temperature of 3000 K. The process of cooling proceeds as a series of instantaneous changes in temperature followed by a period of isothermal equilibrium. As the temperature decreases, a point had been reached where the diffusion rates become too small for the system to sample the configuration space adequately in  $10^{-11}$  s. The temperature at which the system exhibits a clear thermodynamic transition associated with configuration arrest is taken as the liquid-to-glass transition temperature. The temperature in this work was scaled using a scaling factor  $\phi$  given as

$$\phi = 1 - 0.5(\Delta t/\tau)[1 - (v_{0i}^2/v_i^2)] \quad (6)$$

where  $\Delta t$  is the time step,  $\tau$  is the coupling time constant which is 1 ps in the present study, and  $v_{0i}$  and  $v_i$  are the initial and final velocities of the particles corresponding to the initial and final temperatures of each run.

Table 1. Glass composition.

Glass composition	Number of atoms			
	Na	O	B	Total
B <sub>2</sub> O <sub>3</sub>	0	429	286	715
Na <sub>2</sub> O-5B <sub>2</sub> O <sub>3</sub>	51	408	255	714
Na <sub>2</sub> O-4B <sub>2</sub> O <sub>3</sub>	62	403	248	713
Na <sub>2</sub> O-3B <sub>2</sub> O <sub>3</sub>	79	395	237	711
Na <sub>2</sub> O-2B <sub>2</sub> O <sub>3</sub>	110	385	220	715
Na <sub>2</sub> O-B <sub>2</sub> O <sub>3</sub>	178	356	178	715

## 2.3. Pressure scaling

At the same temperature trajectory, the pressure was scaled by scaling the coordinates  $r_i$  and the size of the box in every step according to

$$\psi = 1 + \frac{1}{3}(\Delta t/\tau)B(P_0 - P) \quad (7)$$

where  $P = \frac{2}{3}V(0.5mv_i^2 - \omega)$ ,  $V$  is the volume of the box,  $B$  is the isothermal compressibility derived from the isothermal run and  $\omega$  is the virial coefficient given as

$$\omega = -0.5 \sum_{i \neq j}^N r_{ij} F_{ij}. \quad (8)$$

The coupling constant in this case was chosen to be 10 ps.

The structure of the glass and liquid is characterized by a set of order parameters  $\{q_i\}$  which relax exponentially directly after disturbance. These parameters can be found to satisfy the relations

$$g_{VT}^i = (\partial V/\partial q_i)(\partial H/\partial q_i)/(a_i TV \Delta \alpha) \quad (9)$$

$$g_{VP}^i = (\partial V/\partial q_i)(\partial V/\partial q_i)/(a_i V \Delta K) \quad (10)$$

$$g_{HT}^i = (\partial H/\partial q_i)(\partial H/\partial q_i)/(a_i TV \Delta C_p) \quad (11)$$

where the  $g_{xy}^i$ -values are weighting coefficients describing the relaxation of volume  $V$  or enthalpy  $H$  response to the  $P$  or  $T$  jump and related to the  $\Pi$  ratio by the formula

$$\Pi = (g_{VT}^i)^2 / (g_{HT}^i)(g_{VP}^i). \quad (12)$$

The partial derivatives in equations (9)–(11) were evaluated after the system reaches its equilibrium state.

The isobaric–isothermal vitrification, as reported by Woodcock *et al* [16], was carried out to determine the thermodynamic parameters  $\alpha = (1/V)(\partial V/\partial t)_P$ ,  $C_P = T(\partial S/\partial T)_P$  and  $K = -(1/V)(\partial V/\partial P)_T$ .

### 3. Results

The most remarkable aspect of computer simulations is that complete information on the atomic configuration is available. The important point therefore is how to extract meaningful information from the total knowledge of atomic distribution. Of several thermodynamic parameters, we have examined the glass transition temperature  $T_g$  and the excesses of specific heat, thermal expansion and thermal compressibility at  $T_g$  for  $B_2O_3$  and borate glasses.

Figure 1 illustrates the changes in the volume of  $B_2O_3$  during cooling from 3000 to 300 K and also for heating from 300 to 2000 K by the same scaling factors. Similar behaviour can be observed for the other borate glasses. Decreasing the temperature causes a regular decrease in the volume to a certain temperature  $T_1$  at which a kink in the  $V$  versus  $T$  curve was observed. Starting from 300 K and increasing the temperature to 2000 K produces a kink at the melting point  $T_2$ . The glass transition temperature is considered as the midpoint between  $T_1$  and  $T_2$  and is denoted  $T_g$ .

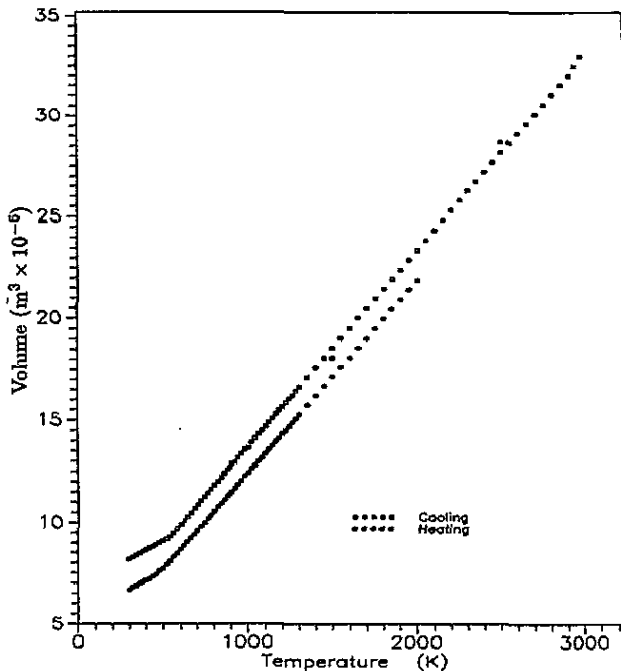


Figure 1. Volume as a function of temperature for  $B_2O_3$  glass.

The calculated values for the specific heat, thermal expansion coefficient and thermal compressibility for the systems studied at both  $T_1$  and  $T_2$  are given in table 2.

Figure 2 shows the changes in the ratio  $\Pi$  as a function of the glass composition, i.e. the alkali oxide content. It is found that the values of  $\Pi$  for  $B_2O_3$  glass at  $T_1$  and  $T_2$  are 4.59 and 4.43, respectively. A decrease in these values was observed on increasing the concentration of alkali oxide to 33.3 mol% and then, an increase in  $\Pi$  occurs on further increase in alkali oxide content.

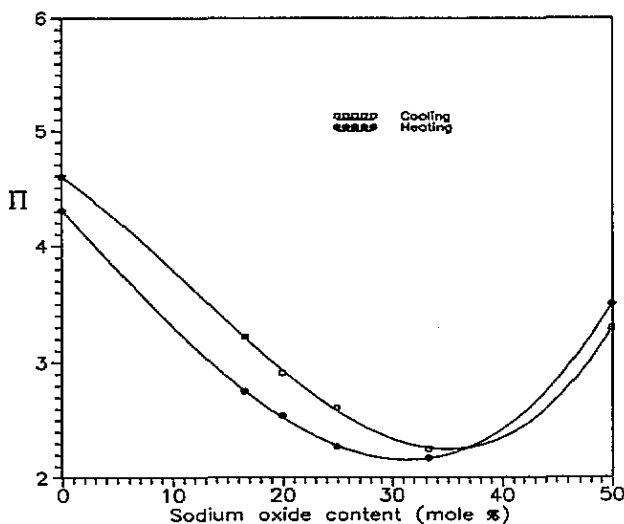


Figure 2. Dependence of the Prigogine-Defay ratio on the alkali oxide content in borate glasses.

#### 4. Discussion

For systems at equilibrium, changes in  $T$  and/or  $P$  lead to changes in the number of order parameters. There is a possibility that the order parameter remains constant if the changes are carried out very rapidly. A successful way to change  $T$  and/or  $P$  rapidly is the use of MD simulations. Freezing in the order parameters by a fast computer experiment generates glasses with an entropy and volume which differ from those of the liquid. When the melt approaches the transition range, the configurational motion becomes very slow and the fluctuation associated with this motion varies slowly with time. A glass will be formed in a configurational state which is associated with the minimum potential energy.

The results in our simulations are given in figure 1, as an example, in which the volume  $V$  of the system is presented as a function of temperature  $T$ . When the quench rate is as high as  $1 \times 10^{12} \text{ K s}^{-1}$ , no crystallization can be detected. Instead, the volume decreases continuously as shown in figure 1. It is also noted that the derivative of the  $V$  versus  $T$  curve changes in a clear-cut way in the glass transition range. In this range the atoms in the glass are fixed at the stable equilibrium position about which they perform collective vibrations. The glass transition range is not a sharp point as occurs in an equilibrium phase transition because there are slow relaxation processes occurring at temperatures well below the transition point. So, the difference between  $T_1$  and  $T_2$  may be attributed to such secondary relaxation.

Table 2. The excess in thermodynamic parameters at the glass transition temperature for  $B_2O_3$  and borate glasses.

Quantity (units)	Value for the following glass compositions					
	$B_2O_3$	$Na_2O-5B_2O_3$	$Na_2O-4B_2O_3$	$Na_2O-3B_2O_3$	$Na_2O-2B_2O_3$	$Na_2O-B_2O_3$
$T_1$ (K), cooling	535	679	716	765	841	931
$T_2$ (K), heating	576	701	740	782	855	962
$V_1$ ( $m^3 mol^{-1}$ )	$7.77 \times 10^{-6}$	$8.09 \times 10^{-6}$	$8.47 \times 10^{-6}$	$8.87 \times 10^{-6}$	$9.05 \times 10^{-6}$	$9.21 \times 10^{-6}$
$V_2$ ( $m^3 mol^{-1}$ )	$8.43 \times 10^{-6}$	$8.41 \times 10^{-6}$	$8.64 \times 10^{-6}$	$9.11 \times 10^{-6}$	$9.33 \times 10^{-6}$	$9.56 \times 10^{-6}$
$(\Delta C_P)_1$ ( $J mol^{-1} K^{-1}$ )	10.34	11.01	12.37	13.66	14.17	13.35
$(\Delta C_P)_2$ ( $J mol^{-1} K^{-1}$ )	10.79	11.62	12.83	13.94	15.03	14.77
$(\Delta \alpha)_1$ ( $K^{-1}$ )	$3.69 \times 10^{-4}$	$4.09 \times 10^{-4}$	$4.65 \times 10^{-4}$	$5.00 \times 10^{-4}$	$5.55 \times 10^{-4}$	$6.16 \times 10^{-4}$
$(\Delta \alpha)_2$ ( $K^{-1}$ )	$4.15 \times 10^{-4}$	$4.53 \times 10^{-4}$	$5.08 \times 10^{-4}$	$5.45 \times 10^{-4}$	$6.13 \times 10^{-4}$	$6.61 \times 10^{-4}$
$(\Delta K)_1$ ( $m^2 N^{-1}$ )	$0.251 \times 10^{-9}$	$0.334 \times 10^{-9}$	$0.416 \times 10^{-9}$	$0.471 \times 10^{-9}$	$0.622 \times 10^{-9}$	$0.994 \times 10^{-9}$
$(\Delta K)_2$ ( $m^2 N^{-1}$ )	$0.343 \times 10^{-9}$	$0.398 \times 10^{-9}$	$0.477 \times 10^{-9}$	$0.537 \times 10^{-9}$	$0.716 \times 10^{-9}$	$1.08 \times 10^{-9}$

Bypassing crystallization during cooling, it is found that the liquid experiences a glass transition which is characterized by abrupt changes in the thermodynamic properties over a relatively small temperature range. Gupta and Moynihan [6] and Moynihan *et al* [7] found experimentally that the Prigogine–Defay ratio for  $B_2O_3$  glass is greater than unity, which indicates that the number of order parameters is more than one. In the present study using MD simulations we came to the same conclusion. This ratio for  $B_2O_3$  glass is found to be of the same order as those obtained experimentally.

The more remarkable aspect in this work is the relation between the ratio  $\Pi$  and the structure of glass (figure 2). It is established that the addition of  $Na_2O$  to the glass causes the planar  $BO_3$  to convert to  $BO_4$  tetrahedra through the formation of pentaborate units. Hence the value of  $\Pi$  is related to the number of order parameters; thus the conversion from three-coordinated to four-coordinated boron is associated with the decrease in the number of order parameters. A further decrease in the value of  $\Pi$  is associated with the formation of tetraborate, triborate and diborate units successively. The structure of glass at an  $Na_2O$  concentration of 33.3 mol% is mainly diborate units. It is established that presence of diborate groups in the network increases the coherence of the structure. The minimum value of  $\Pi$  and consequently the minimum number of order parameters can be considered as an indication that the structure of glass is mainly built up from diborate units. However, the value of  $\Pi$  is still far from unity, i.e. the number of order parameters is larger than one. For higher concentrations of alkali oxide in the glass, the  $BO_4$  groups start to break down to form  $BO_3$  groups with non-bridging oxygen ions. This behaviour is associated with an increase in the value of  $\Pi$ . Since the values of  $\Pi$  fluctuate but do not reach unity for borate glasses, one can say that the formation of non-bridging oxygen ions starts even during the formation of diborate groups.

## 5. Conclusions

The following conclusions can be drawn.

- (i) There is no way to freeze in the order parameter without the use of a very rapid method to change the temperature or the pressure.
- (ii) The Prigogine–Defay ratio can be used to examine the structure of glass as it is related to the number of order parameters.
- (iii) The change in the value of  $\Pi$  indicates that the formation of non-bridging oxygen ions takes place during the formation of diborate groups.

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