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## Prigogine–Defay Ratio for an Ionic Glass-Former: Molecular Dynamics Simulations

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The pressure dependence of the glass-transition temperature,  $T_g(P)$ , of the ionic glass-former  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$ , CKN, has been obtained by molecular dynamics (MD) simulations. The liquid–glass difference of thermal expansivity,  $\Delta\alpha$ , heat capacity,  $\Delta C_p$ , and isothermal compressibility,  $\Delta\kappa$ , have been calculated as a function of pressure. It has been found that the Ehrenfest relation  $dT_g/dP = TV\Delta\alpha/\Delta C_p$  predicts the pressure dependence of  $T_g$ , but the other Ehrenfest relation,  $dT_g/dP = \Delta\kappa/\Delta\alpha$ , does not. Consequently, the Prigogine–Defay ratio,  $\Pi = \Delta C_p \Delta\kappa / TV\Delta\alpha^2$ , is  $\Pi \sim 1.2$  at low pressures, but increases 1 order of magnitude at high pressures. The pressure dependence of the Prigogine–Defay ratio is interpreted in light of recent explanations for the finding  $\Pi > 1$ .

## I. Introduction

A liquid reaches a metastable equilibrium state when the temperature decreases below the melting temperature  $T_m$ , but the thermodynamically stable crystalline state is not formed. If the temperature of the supercooled liquid is further reduced, the system will become an amorphous solid at the glass transition temperature  $T_g$ , which is typically  $T_g \sim 2/3 T_m$ .<sup>1–3</sup> The very long relaxation times below  $T_g$ , in comparison to the actual measurement times, keep the system in a nonequilibrium glassy state. In contrast with the equilibrium phase transition at  $T_m$ , for which thermodynamic properties such as volume  $V$ , entropy  $S$ , and enthalpy  $H$  experience abrupt changes, the temperature dependence of these properties display only a change of slope at  $T_g$ . Therefore, at  $T_g$ , one observes abrupt changes only in those thermodynamical functions related to derivatives of these properties, such as the isobaric thermal expansivity,  $\alpha = 1/V(\partial V/\partial T)_P$ , the isobaric heat capacity,  $C_p = (\partial H/\partial T)_P$ , and the isothermal compressibility,  $\kappa = -1/V(\partial V/\partial P)_T$ . Since  $V$  and  $H$  are related to first derivatives of the Gibbs free energy, then  $\alpha$ ,  $C_p$ , and  $\kappa$  are related to second derivatives of the Gibbs free energy. Thus, if the equilibrium thermodynamics concepts are applied to the glass transition, it would be classified as a second-order phase transition according to the Ehrenfest definitions. In case of first-order phase transitions, such as the melting process taking place at  $T_m$ , the Clapeyron equation  $dP/dT = \Delta S/\Delta V$  predicts the coexistence curve (here  $\Delta X$  indicates the difference between the values of property  $X$  for the two phases). Consequently, if one consider the glass-transition as an equilibrium second-order phase transition, the coexistence curve for the glass and the supercooled liquid would be given by the Ehrenfest relations:<sup>1–6</sup>

$$\frac{dT_g}{dP} = \frac{\Delta\kappa}{\Delta\alpha} \quad (1)$$

$$\frac{dT_g}{dP} = \frac{TV\Delta\alpha}{\Delta C_p} \quad (2)$$

(now  $\Delta X = X(\text{liquid}) - X(\text{glass})$ ). For equilibrium second-order transitions, both eqs (1) and (2) are satisfied, and the so-called Prigogine–Defay (PD) ratio,

$$\Pi = \frac{\Delta C_p \Delta\kappa}{TV\Delta\alpha^2} \quad (3)$$

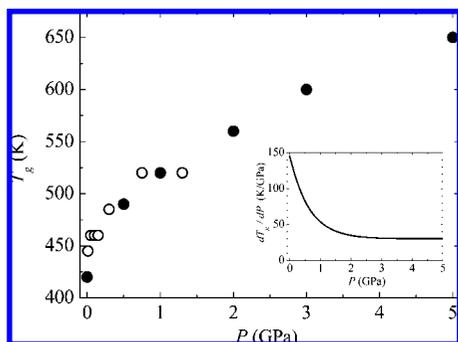
is  $\Pi = 1$  at the transition.

As the equilibrium second order phase transition theory cannot be applied to the glass-transition, one expect deviation from eqs 1 and 2, and, consequently, one expects that the Prigogine–Defay ratio differs from one. Experimentally, it is observed that eq 2 is normally satisfied, whereas eq 1 is not, so that the usual result is  $\Pi > 1$ . Davies and Jones<sup>7,8</sup> showed that the condition  $\Pi > 1$  is an indication that the thermodynamic properties of the glass are not uniquely determined by the variables  $P$  and  $T$ , instead a number of order parameters,  $z_i = z_i(P, T)$ , are also needed to specify the state, for instance,  $V = V(T, P, \{z\})$ . In the liquid phase at equilibrium, the Gibbs free energy,  $G = G(T, P, \{z\})$ , is such that  $\partial G/\partial z_i = 0$ , so that the glass transition takes place when these order parameters  $z_i(T, P)$  freeze in and remain constant in the glassy state.<sup>7,8</sup>

The PD ratio has been measured for several polymers, molecular, ionic, and metallic glass-formers (see the review of  $\Pi$  values in Table 1 of ref 9). Although molecular dynamics (MD) simulation has become a fundamental tool in studying thermodynamics, structural, and dynamic issues concerning the glass transition, only few MD studies have been reported dealing with the calculation of the PD ratio. In an early MD study by Clarke,<sup>10</sup> the value  $\Pi = 1$  has been obtained for a Lennard-Jones model for argon. Meikhail<sup>11</sup> performed MD simulations of borate glasses, and he found that  $\Pi$  decreases from 4.5 to 2.2 while the amount of  $\text{Na}_2\text{O}$  in  $\text{B}_2\text{O}_3$  increases from zero to 35%. Morineau et al.<sup>12</sup> obtained  $\Pi = 1.17$  by Monte-Carlo simulations of meta-xylene. Speedy<sup>13</sup> revised the PD ratio and

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**Figure 1.** Pressure dependence of the glass transition temperature obtained by MD simulations of CKN. Previous data are given by black circles,<sup>16</sup> and new data of this work are given by white circles. The inset shows the corresponding derivative  $dT_g/dP$ .

provided tests through MD simulations of a tetravalent network model. Recently, Pedersen et al.<sup>14</sup> defined a dynamic PD ratio given by time correlation functions of energy and pressure fluctuations, analogous to early proposal by Jackle<sup>15</sup> for fluctuations at the long-wavelength limit. The two model systems simulated in ref 14 indicated  $\Pi \sim 1$  within a large frequency range, but these MD simulations concerned fluctuations occurring only in the metastable equilibrium supercooled liquid and not the nonequilibrium glassy state.

In a previous work,<sup>16</sup> the dynamics of the ionic glass-former  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$ , CKN, was investigated by MD simulations as a function of temperature at six different pressures from room pressure up to 5.0 GPa. CKN is a well-known glass-former for which an extensive literature is available on thermodynamic properties, equilibrium structure, and dynamics. There are some early experimental data available for CKN under pressure,<sup>17,18</sup> however, up to 0.2 GPa, which is a much narrower range than investigated by the MD simulations.

The goal of this work is to provide a detailed analysis of the dependence  $T_g(P)$  observed in the previous work<sup>16</sup> aiming to verify the Ehrenfest relations and the PD ratio and to study how these relations change as a function of pressure.

The  $T_g(P)$  data given in ref 16 are shown in Figure 1 by black circles. It was already shown that the MD results follow a well-known empirical  $T_g(P)$  relationship observed in many glass-formers (see Figure 1 of ref 16). In this work, more MD simulations were needed for other pressures in order to evaluate  $\Delta\kappa$  with reasonable accuracy. The new  $T_g(P)$  data of this work are shown in Figure 1 by the white circles, so that a whole of 14 different pressure conditions have been simulated. The aim of this work is to compare the MD result for  $dT_g/dP$  (see the inset of Figure 1) with the prediction of eqs 1 and 2, in which all of the properties  $\Delta\alpha$ ,  $\Delta C_p$ , and  $\Delta\kappa$  are consistently calculated from the MD simulations for the same model. Thus, this work provides the pressure dependence of the PD ratio for the CKN model. The main result is that  $\Pi$  is close to 1 at room pressure, but larger than 10 at high pressures. The literature on the theoretical meaning of the PD ratio is briefly reviewed in the next subsection, in particular recent proposals<sup>9</sup> from which the actual value of  $\Pi$  is not related to the number of order parameters needed to describe the properties of the glass.

## II. Theoretical Background

Goldstein<sup>19</sup> derived eqs 1 and 2 with the assumption that a single order parameter,  $z = z(T, P)$ , determines the excess thermodynamic quantities. Following the work of Davies and Jones,<sup>7,8</sup> he assumed that  $z$  freezes in at the glass transition

temperature upon cooling the system. In case there is a unique relationship between  $z$  and any given excess function, say the excess volume  $V_e$ ,  $V_e$  itself could be chosen as the parameter which determines the glass transition once  $V_e$  reaches a critical value. The temperature and pressure dependence  $dV_e = V\Delta\alpha dT - V\Delta\kappa dP$  implies eq 1 at constant  $V_e$  along a  $T_g(P)$  line. Thus, in case that  $V_e$  determines the glass transition, the validity of eq 1 will be consistent with free-volume theories.<sup>2,3</sup> On the other hand, if the relevant excess function is the entropy  $S_e$ , eq 2 is valid rather than eq 1. The same eq 2 results if one considers that the glass transition is determined by the freeze in of the excess enthalpy  $H_e$ . The experimental data reviewed by Goldstein<sup>19</sup> indicate that eq 2, and not eq 1, is fulfilled, prompting the conclusion that free-volume is not the crucial variable in determining the glass transition. However, the appropriateness of eq 2 does not allow one to distinguish between  $H_e$  or  $S_e$  based theories for the glass transition.

In a subsequent paper, Goldstein<sup>20</sup> criticized further attempts on validating eq 1 based on different definitions of the glass compressibility  $\kappa_g$  or on the assumption that  $V_e$  continues to decrease below  $T_g$ . If pressure is released from a glass prepared at high  $P$ , the resulting  $V$  will not be the same of the glass prepared at low  $P$ . Thus, a glass prepared at higher pressure has different volume at a given  $P$  and  $T$ . In other words, the adequacy of eqs 1 and 2 could be stated as the question whether glasses prepared by cooling under different pressures will have the same  $V_e$  or  $S_e$  (or  $H_e$ ). Therefore, the experimental finding that eq 2 is fulfilled indicates that glasses prepared at different pressures have the same excess entropy (or enthalpy) at a given  $P$  and  $T$  below the transition.

Speedy<sup>13</sup> derived the first Ehrenfest relation with the explicit  $z$  dependence on the volume of the glass,  $V_g = V_g(T, P, z)$ , so that eq 1 would have a correction term:

$$\frac{dT_g}{dP} = \frac{\Delta\kappa + \delta V_p/V}{\Delta\alpha} \quad (4)$$

where  $\delta V_p$  accounts to the fact that  $z$  is different for glasses prepared at different pressures:

$$\delta V_p = \frac{V_g(T, P, z(P_1)) - V_g(T, P, z(P_2))}{P_1 - P_2} \quad (5)$$

In the above equation,  $V_g = V_g(T, P, z(P_i))$  is the volume of a glass of kind  $z(P_i)$ , i.e. a glass made by cooling the liquid at  $P_i$  for which the order parameter is frozen at  $z(P_i)$ . The  $\Delta\kappa$  in eq 1 can be redefined with the correction term  $\delta V_p$  included. The definition of  $\delta V_p$  by eq 5 makes eq 4 correct. An analogous correction term  $\delta H_T$  could be added to eq 2,<sup>13</sup> but the fact that eq 2 is generally valid means that  $\delta H_T$  is negligible.

The first issue addressed in this work is which of the Ehrenfest relation is valid for the CKN model. It will be shown that eq 1 is not valid within the whole range of pressure investigated, so that the second issue here is the magnitude of the PD ratio, eq 3. The finding  $\Pi > 1$  suggests that the hypothesis of a single order parameter is not correct, instead two or more order parameters would be needed to describe the glass. In the case that more than one order parameter is needed to describe the glass, Davies and Jones obtained:<sup>7,8</sup>

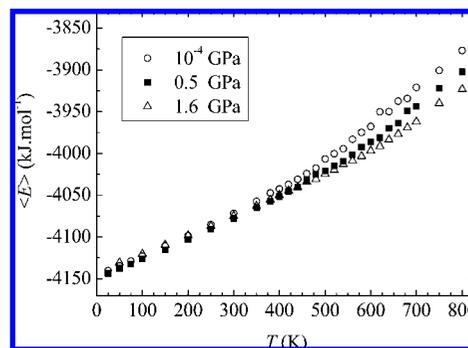
$$\frac{\Delta\kappa}{\Delta\alpha} > \frac{TV\Delta\alpha}{\Delta C_p} \quad (6)$$

However, Di Marzio<sup>21</sup> showed that an equality, rather than an inequality, holds in eq 6 for any number of order parameters. Thus, the finding  $\Pi > 1$  would imply that the very concept of instantaneous freeze in of order parameters should not apply. Di Marzio's conclusion has been criticized by Goldstein<sup>22</sup> and Gupta and Moynihan.<sup>23</sup> Goldstein<sup>22</sup> argued that the Di Marzio conclusion relies on the assumption that both the  $\Delta V$  and the  $\Delta S$  are zero at the glass transition, so that  $\Pi > 1$  is not a consequence that the order parameter concept should be ruled out, instead it is due to the fact  $\Delta V \neq 0$  at the glass transition. Thus, Goldstein returns to the argument that two glasses at same  $(T, P)$ , but with different histories, i.e. different  $z_i$  and  $z_j$ , do not have the same volume,  $V(T, P, z_i) \neq V(T, P, z_j)$ . Gupta and Moynihan<sup>23</sup> showed that  $\Pi = 1$  for more than one order parameter as long as the constraint  $(\partial V/\partial z_i)/(\partial S/\partial z_i) = (\partial V/\partial z_j)/(\partial S/\partial z_j)$  applies. In the case that this constraint does not hold, more than one order parameter gives  $\Pi > 1$ . (If there is only one order parameter,  $\Pi = 1$  irrespective of this constraint). Although  $\Pi > 1$  does not contradict the order parameter concept, it does not prove that the concept of freeze in  $\{z_i\}$  at  $T_g$  must be applicable. In Di Marzio's comment<sup>24</sup> on Gupta and Moynihan paper,<sup>23</sup> instead of an abrupt freeze in of  $\{z_i\}$  at  $T_g$ , a more general approach was proposed by a time-dependent order parameter theory which accounts for  $dz_i/dt$ .

More recently, Schmelzer and Gutzow<sup>9</sup> derived the PD ratio by using concepts of thermodynamics of irreversible processes. In contrast to previous approaches, the (single) order parameter does not freeze in at a sharp temperature. Instead, there is a finite temperature interval in which the order parameter changes smoothly from the equilibrium value to the nonequilibrium final value.<sup>9,25</sup> The system remains in the glassy state because the change of  $z$  to equilibrium is very slow at low  $T$ , i.e. beyond measurement time. Within this framework, the general result is  $\Pi > 1$  for glasses prepared by cooling processes. The interpretation of PD ratio in this approach is different from the previous papers, since the finding  $\Pi > 1$  does not imply that the glass must be described by more than one order parameter. The result  $\Pi > 1$  is due to an affinity contribution,  $A = -(\partial G/\partial z)_{T,P}$ , in the denominator of eq 3, which is negative for cooling processes, implying that  $z \geq z_{eq}$ , where  $z_{eq}$  is the equilibrium value of the order parameter.<sup>9,25</sup> In the case of MD simulations of glass transition, where the very high cooling rate implies that the transition takes place in a rather extended temperature interval, we believe that the concept of an order parameter which changes continuously within a temperature interval, rather than an abrupt freeze in at a sharp  $T_g$ , is more representative of the real situation.

### III. Computational Details

Details on the CKN model and the MD simulation protocol have been already given in the previous publication,<sup>16</sup> so that only brief remarks are provided here. The CKN model is based on a pair wise Born–Mayer potential energy function.<sup>26,27</sup> The system was simulated in a cubic box containing 501 ions (292  $\text{NO}_3^-$ , 83  $\text{Ca}^{2+}$ , and 126  $\text{K}^+$ ). Fourteen different pressures were considered from  $10^{-4}$  to 5.0 GPa. Temperature and pressure were controlled by the method of Berendsen et al.<sup>28</sup> We performed the same cooling procedure of ref 16 for the new pressure conditions simulated in this work. Starting from well-equilibrated liquid configurations at 800 K, the temperature was reduced in steps of 20 K when close to  $T_g$ , and 50 K when far from  $T_g$ , down to ca. 50 K. For each  $(P, V, T)$  state, the simulation lasted for 12.0 ns with a time step of 15.0 fs. The glass transition



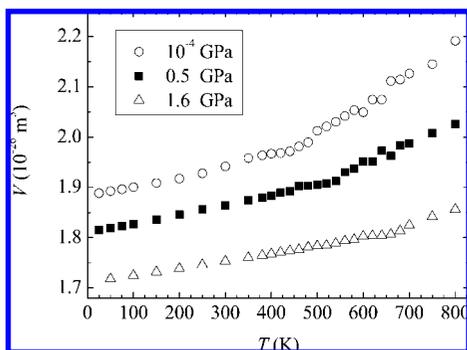
**Figure 2.** Temperature dependence of the average potential energy obtained by MD simulations of CKN at three different pressures.

temperature for each pressure was obtained from plots of volume vs temperature,  $V(T)$ , and also potential energy vs temperature,  $E(T)$ .

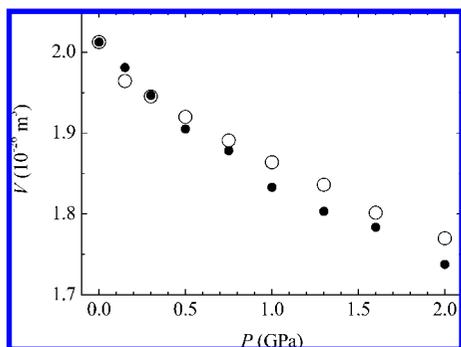
The experimental value reported by Angell et al.<sup>17</sup> is  $dT_g/dP \sim 60 \text{ K GPa}^{-1}$  at the low- $P$  limit. The MD results shown in the inset of Figure 1 indicate that the calculated  $dT_g/dP$  is close to experiment only at  $P \sim 0.8 \text{ GPa}$ , whereas the calculated low- $P$  limit is ca. twice the experiment. We assign the difficulty in calculating accurate  $dT_g/dP$  values at low- $P$  to the fact that the typical magnitude of pressure fluctuations in a MD simulation of a relatively small system size is much larger than the average value of  $0.0001 \text{ GPa}$  in the case of room pressure condition. In a given MD simulation of CKN, we found typical standard deviation in pressure of  $\sigma \sim 0.1 \text{ GPa}$ . In order to obtain accurate compressibilities in this work, it is important to perform MD simulations at close spaced pressure conditions. However, two MD cooling performed at different pressures which are too close are not able to distinguish any significant difference on  $T_g$  (see the white symbols at low pressures in Figure 1). In other words, there is a compromise of running MD simulations at large enough pressure gap so that distinct average pressures are achieved beyond the magnitude of fluctuations, but not too different pressures so that the calculation of compressibility by finite difference would be too rough. In addition, it is well-known that the high cooling rate in MD simulations gives  $T_g$  which is higher than experiment (in case of CKN at room pressure, the experimental value is  $T_g = 335 \text{ K}$ ).<sup>17</sup> Nevertheless, we stress that the issue here is the self-consistent comparison between  $dT_g/dP$  and the prediction of the Ehrenfest relations as the result of MD simulations for a given model at a given cooling rate.

### IV. Results and Discussion

Figure 2 illustrates, for three different pressures, the temperature dependence of the average potential energy,  $\langle E \rangle$ , of the CKN model. It is clear from Figure 1 that  $\langle E \rangle$  is different for the high temperature liquid phase at different pressures, and that  $\langle E \rangle$  is almost the same for the corresponding glasses. In contrast, the temperature dependence of the average volume for these same pressures (Figure 3) indicates that the glasses are formed with very different volumes for each pressure condition. From the slopes of these plots one obtains the heat capacity,  $C_P = (\partial H/\partial T)_P$ , where the enthalpy is  $H = U + PV$ ,  $U$  is the total energy, and the thermal expansivity,  $\alpha = 1/V(\partial V/\partial T)_P$ , for both the liquid and the glass, so that the differences  $\Delta C_P$  and  $\Delta \alpha$  in eq 2 can be evaluated. In order to test eq 1, the difference of isothermal compressibility,  $\kappa = -1/V(\partial V/\partial P)_T$ , must be also calculated. Following vertical lines on the results illustrated in Figure 3, i.e. isothermic paths, for all of the simulated pressures,



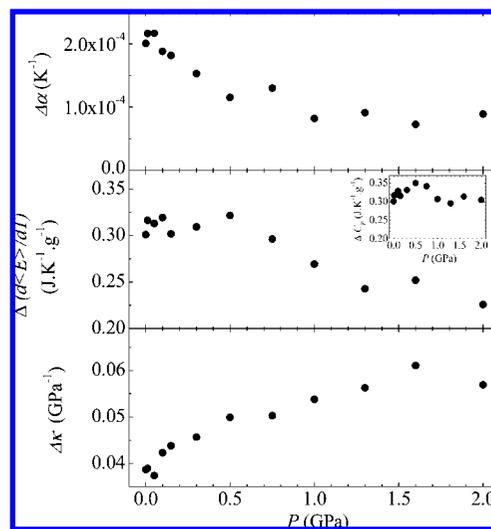
**Figure 3.** Temperature dependence of the average volume obtained by MD simulations of CKN at three different pressures.



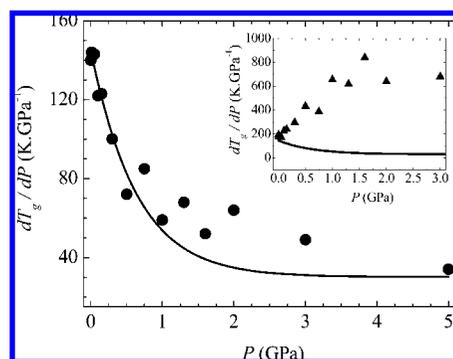
**Figure 4.** Pressure dependence of the average volume obtained by MD simulations of CKN at 500 K. Data shown by black circles correspond to cooling MD simulations performed at different pressures starting at high temperature. Data shown by white circles correspond to MD simulations performed at fixed  $T = 500$  K with increasing pressure starting at room pressure.

one obtains the pressure dependence of the volume at any chosen temperature. The resulting  $V(P)$  curve is illustrated by black circles in Figure 4 for  $T = 500$  K, whose slope at low and high pressures gives, respectively, the compressibility for liquid and glassy phases. According to Nieuwenhuizen,<sup>29</sup> this is the correct way of evaluating  $\Delta\kappa$  in a consistent way to check the validity of eq 1. Figure 4 shows by white circles another path from which a  $V(P)$  curve could be also obtained: the start configuration was the liquid at room pressure and  $T = 500$  K, then, a sequence of MD simulations was performed with increasing pressure while keeping the temperature fixed. It is clear from Figure 4 that both the paths give similar  $V(P)$  at low pressures, i.e. for the equilibrium liquid phase. However, when the system is first cooled to 500 K at room pressure, and then pressure is increased, the resulting  $V(P)$  curve follows slightly higher values at the glassy phase than through cooling protocols at different pressures. Nevertheless, the slopes of the  $V(P)$  plots shown in Figure 4 for these different glasses, and thus their compressibilities, are very similar.

All of the differences on thermodynamic quantities needed to evaluate eqs 1 and 2 are shown in Figure 5 for CKN as a function of pressure. The  $\Delta\alpha$  and the difference on the derivative of the potential energy,  $\Delta(\partial\langle E \rangle / \partial T)_P$ , decreases with increasing pressure up to 1.0 GPa, and then remains almost constant. However,  $\Delta C_P$  does not have a clear trend with pressure (see the inset of the middle panel of Figure 5). The bottom panel of Figure 5 shows that  $\Delta\kappa$  increases with pressure until it reaches an almost constant value at high pressures. The  $\Delta\kappa$  increases with pressure because each isothermic condition corresponds to a higher  $T_g$  when pressure increases (see Figure 1). Thus, despite the increase of pressure,  $\Delta\kappa$  is higher at high  $P$  due to



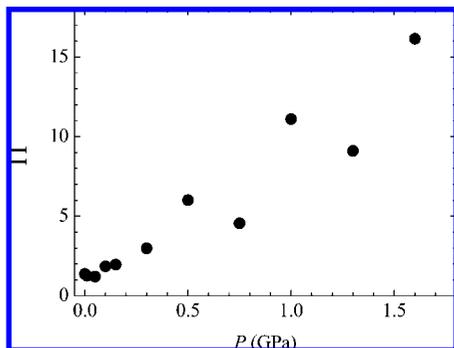
**Figure 5.** Pressure dependence of the difference between liquid and glass values for thermal expansivity (top panel), the derivative of potential energy (middle panel), and compressibility (bottom panel) obtained by MD simulations of CKN. The inset in the middle panel gives the pressure dependence of  $\Delta C_P$ .



**Figure 6.** Comparison between  $dT_g/dP$  calculated by MD simulations (full line, see inset of Figure 1) and the prediction of the Ehrenfest relation  $dT_g/dP = TV\Delta\alpha/\Delta C_P$  (black circles, eq 2). The inset shows the prediction of the other Ehrenfest relation  $dT_g/dP = \Delta\kappa/\Delta\alpha$  (black triangles, eq 1) and the MD data (full line).

the increase of  $T_g$ . Gupta and Moyhinan<sup>23</sup> also considered CKN in the experimental validation of the Ehrenfest equations. At room pressure, they used the experimental data  $\Delta\alpha = 2.3 \times 10^{-4} \text{ K}^{-1}$ ,  $\Delta C_P = 0.54 \text{ J K}^{-1} \text{ g}^{-1}$ , and  $\Delta\kappa = 0.069 \text{ GPa}^{-1}$ .<sup>23</sup> Although there is not a quantitative agreement between the experimental data and the MD result at room pressure (see Figure 5), the order of magnitude of the MD results are in reasonable agreement with experiment.

With all of the differences on the thermodynamics quantities provided in Figure 5, together with the corresponding temperature and volume at the glass transition, the Ehrenfest relations can be tested as a function of the pressure. The appropriateness of eq 2 for the MD results of CKN is shown in Figure 6. The prediction of the Ehrenfest relation, eq 2, is given by the black circles, whereas the MD result for  $dT_g/dP$ , as given in the inset of Figure 1, is shown by the full line. It is necessary many cooling simulations for each pressure starting from different initial configurations in order to evaluate the most important source of uncertainty. Nevertheless, uncertainties can be appreciated from the scatter in the data. Bearing in mind the natural difficulty in obtaining all of the necessary quantities, the appropriateness of eq 2 is reasonable. The adequacy of eq 2 is more striking when one compares with the corresponding

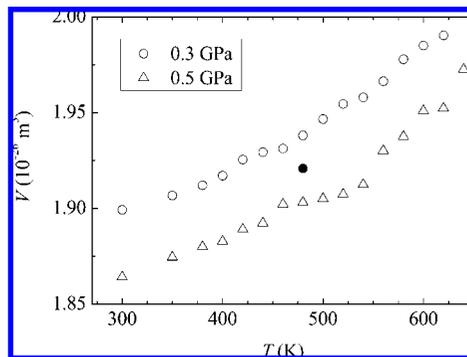


**Figure 7.** Pressure dependence of the Prigogine–Defay ratio,  $\Pi = \Delta C_p \Delta \kappa / TV \Delta \alpha^2$ , obtained by MD simulations of CKN.

pressure dependence of  $dT_g/dP$  as predict by eq 1 (inset of Figure 6). It is clear that the eq 1 prediction for the CKN model is that  $dT_g/dP$  increases with pressure, whereas the actual MD result is the opposite trend. Figure 7 shows the PD ratio calculated for the CKN model as a function of pressure. Both eqs 1 and 2 provide a reasonable prediction for  $dT_g/dP$  at the room temperature limit, so that  $\Pi \sim 1.2$  at low pressures. However, the PD ratio increases by more than 1 order of magnitude for  $P > 1.0$  GPa. The experimental finding for CKN is  $\Pi = 4.5$  at room pressure.<sup>23</sup>

In a previous investigation of borate glasses by MD simulations,<sup>11</sup> it has been found that the PD ratio decreases with increasing amount of  $\text{Na}_2\text{O}$  in  $\text{B}_2\text{O}_3$ . Interpreting the magnitude of the PD ratio as an indication of the number of order parameters, the authors of ref 11 assign smaller  $\Pi$  values at high  $\text{Na}_2\text{O}$  concentration to the conversion from tetraborate to triborate and diborate units successively. In contrast, in this work we are dealing with the same CKN model and the remarkable change on the PD ratio is the result of changing pressure. Thus, we do not interpret the pressure dependence of the PD ratio as a signature of changes on the number of order parameters needed to describe the glass. The Schmelzer and Gutzow approach<sup>9</sup> seems more useful to interpret the pressure dependence of the PD ratio for the CKN model. In refs 9 and 25, a single order parameter description results  $\Pi > 1.0$  proper to the assumption that the order parameter does not freeze in at a sharp temperature. The change on  $z$  during the temperature interval which encompasses the glass transition is the reason for  $\Pi > 1$ . Within this picture, it becomes reasonable that the MD simulations of CKN give  $\Pi$  close to 1 at low pressures, but high  $\Pi$  at high pressures, which would need very much longer simulation time than the low pressure simulations.

The above interpretation of the pressure dependence of the PD ratio for the CKN model on the basis of the kinetics of the variation of the order parameter implies that the explicit calculation by MD simulations of the  $\delta V_p$  term in eq 4 eventually could not correct the prediction of the first Ehrenfest relation, even though  $\delta V_p$  has been defined in eq 5 in order to make eq 4 formally exact.<sup>13</sup> Figure 8 illustrates the calculation of  $\delta V_p$  by the MD simulations of CKN for a pair of pressure conditions. The white symbols in Figure 8 give the temperature dependence of the volume during cooling processes at  $P_1 = 0.3$  GPa and  $P_2 = 0.5$  GPa. Then, the configuration of the glass prepared at  $P_2$  at  $T = 480$  K, which corresponds to  $T_g(P_1)$ , is the starting configuration of a new MD simulation in which the pressure is reduced from  $P_2$  to  $P_1$ . The resulting volume after the relief of pressure from  $P_2$  to  $P_1$  is indicated by the black circle in Figure 8, from which we calculated the difference between the volume of glasses of kind  $z(P_1)$  and  $z(P_2)$  at



**Figure 8.** White symbols showing the temperature dependence of the average volume obtained by MD simulations of CKN at two different pressures. The single black circle is the resulting volume after the glass prepared at 0.5 GPa has experienced a pressure reduction to 0.3 GPa at fixed  $T = 480$  K.

the same  $T = 480$  K and  $P = 0.3$  GPa (see eq 5). The original prediction for  $dT_g/dP = 430$  K  $\text{GPa}^{-1}$  by eq 1 reduces to 350 K  $\text{GPa}^{-1}$  by adding the  $\delta V_p$  term on eq 4. Although the correction is in the right trend, the resulting value is still much higher than the actual MD result or the eq 2 prediction for  $dT_g/dP$  (Figure 6). In light of the temperature dependence of the energy shown in Figure 2, it is clear that the corresponding correction term  $\delta H_T$  would be negligible,<sup>13</sup> so that eq 2 provides a reasonable prediction of  $dT_g/dP$  for CKN simulated at different pressures.

## V. Conclusions

The pressure dependence of the glass transition temperature of the archetypical ionic glass-former CKN has been investigated by MD simulations. The calculated derivative  $dT_g/dP$  decreases from ca. 150 K  $\text{GPa}^{-1}$  at room pressure to ca. 30 K  $\text{GPa}^{-1}$  at 2.0 GPa and then remains almost constant up to 5.0 GPa. In a consistent way, i.e. by using the same configurations resulting from cooling at several pressures, all of the thermodynamic quantities needed to evaluate  $dT_g/dP$  by the Ehrenfest relations were calculated by MD simulations. The equation based on  $\Delta C_p$  and  $\Delta \alpha$ , eq 2, predicts the correct pressure dependence of the MD data for  $dT_g/dP$ . On the other hand, the equation based on  $\Delta \kappa$  and  $\Delta \alpha$ , eq 1, predicts increasing  $dT_g/dP$  with increasing pressure, which is in conflict with the actual  $dT_g/dP$  MD data. At low pressures, both eqs 1 and 2 give reasonable account of  $dT_g/dP$  for the CKN model, so that the PD ratio is close to 1. However, as a consequence of the wrong pressure dependence of  $dT_g/dP$  resulting from eq 1, the calculated PD ratio increases about 1 order of magnitude at 1.0 GPa. Therefore, the appropriateness of eq 2, and not eq 1, strongly suggests that the free-volume concept is not the most relevant concept to describe the glass transition. Since all of the calculations have been performed with the same CKN model, the strong pressure dependence of the PD ratio cannot be interpreted in terms of the number of order parameters needed to describe the glass. Very recent considerations of the PD ratio indicate that the finding  $\Pi > 1$  is not a necessary signature that more than one order parameter is needed to describe the glass.<sup>9,25</sup> The most important modification put forward by Schmelzer and Gutzow<sup>9</sup> is that the (single) order parameter changes continuously from the nonequilibrium value at high  $T$  down to the final out-of-equilibrium value within an interval of temperature, rather than an abrupt freeze in at  $T_g$  as in the classic papers by Davies and Jones.<sup>7,8</sup> Since the glass transition is smeared out in a large interval of temperature in MD experiments, the interpretation

of Schmelzer and Gutzow<sup>9</sup> seems more applicable to the MD results of CKN.

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