

## Fragility and glassy dynamics of $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$ under pressure: Molecular dynamics simulations

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(Received 1 April 2008; accepted 29 April 2008; published online 22 May 2008)

Molecular dynamics simulations of the glass-forming liquid  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$  (CKN) were performed from high temperature liquid states down to low temperature glassy states at six different pressures from  $10^{-4}$  to 5.0 GPa. The temperature dependence of the structural relaxation time indicates that the fragility of liquid CKN changes with pressure. In line with recent proposal [Scopigno *et al.*, *Science* **302**, 849 (2003)], the change on liquid fragility is followed by a proportional change of the nonergodicity factor of the corresponding glass at low temperature. © 2008 American Institute of Physics. [DOI: 10.1063/1.2931525]

The viscosity  $\eta$  of a supercooled liquid increases several orders of magnitude when the system is cooled to the glass transition temperature  $T_g$ , in which an amorphous solid state is reached. Although the temperature dependence of  $\eta$  for the archetypical glass-former  $\text{SiO}_2$  is satisfactorily represented by an Arrhenius law, this is rarely the situation for most of the supercooled liquids.<sup>1</sup> Instead, it is usually observed a nonlinear  $\eta(T)$  dependence in an Arrhenius plot  $\ln(\eta) \times 1/T$ . In order to allow comparisons between systems with very different  $T_g$ , a corresponding-states principle was proposed by normalizing the inverse temperature as  $T_g/T$ .<sup>2</sup> The fragility concept of a supercooled liquid was then introduced as a measure of the departure of the temperature dependence of transport coefficients from a strictly Arrhenius law.<sup>3</sup> One can assign a numerical value for fragility  $m$  as the derivative of such a normalized plot, and it is usually given at the limit  $T \rightarrow T_g$ . By assuming this definition,  $m$  is a measure of the activation energy, measured in  $k_B T_g$  units, for viscous flow at  $T_g$ .

The fact that a supercooled liquid is “fragile” means that the activation energy is not constant, but it is instead temperature dependent. Several theories have been proposed for the origin of a temperature dependent activation energy, for instance, by the temperature dependence of free volume,<sup>4</sup> configurational entropy,<sup>5</sup> or elastic moduli.<sup>6</sup> Theories based on entropy or elastic properties, but not a free volume theory, are consistent with a potential energy barrier picture for viscous flow and structural relaxation of supercooled liquids.<sup>7</sup> In such a picture, a large number of minima in a potential energy surface is available for the system at low temperatures, and relaxation occurs by transitions over potential barriers due to the local rearrangement of atomic coordinates provided that enough thermal energy is available. More recently, properties of the potential energy landscape and a microscopic view of atomic rearrangements have been given by computer

simulations of model systems.<sup>8</sup> Molecular dynamics (MD) simulations of a binary Lennard–Jones mixture demonstrated the connection between the slow relaxation of the supercooled liquid and the underlying energy landscape.<sup>9</sup> The MD simulations indicated that within the same temperature range in which the liquid starts to explore deeper energy minima one also observes the onset of nonexponential relaxation, activated process due to jumps of particles, and fragile behavior.

The connection between structural relaxation of the supercooled liquid and the properties of the potential energy minima experienced by the glass at low temperature has been revealed by inelastic x-ray scattering (IXS) spectroscopy.<sup>10,11</sup> The analysis of IXS spectra provides the nonergodicity factor  $f_q$  for low temperature glasses. The  $f_q$  is the value that the time correlation function of density fluctuations of wave-vector  $q$ , that is, the intermediate scattering function  $F(q, t)$ , reaches at long time in a system in which structural relaxation has been arrested. If the vibrational dynamics of the glass is represented by a harmonic approximation, it can be shown that the inverse of the nonergodicity factor is linearly dependent on temperature  $f_q^{-1} = 1 + \alpha T/T_g$ , in the  $T \rightarrow 0$  and  $q \rightarrow 0$  limit.<sup>10,11</sup> The  $\alpha$  parameter can be expressed in terms of the eigenvalues and eigenvectors of the normal modes used in the harmonic representation of the vibrational dynamics of the glass. The IXS measurements of systems with very different fragilities showed that a linear correlation holds between  $m$  and the  $\alpha$  parameter of the corresponding glass.<sup>11</sup> This finding implies that the characteristic features of energy minima and potential barriers are related to each other.

Previous tests of the model of Ref. 11 were based on plotting experimental  $m$  and  $\alpha$  values for different glass-formers. In a recent MD investigation of binary Lennard–Jones mixtures,<sup>12</sup> the correlation  $m \times \alpha$  has been also observed for three different models with distinct potential energy functions. However, a more stringent test of the model would consider the *same* system for which  $m$  and  $\alpha$

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could be changed. This is the aim of this work: We performed MD simulations in which the model is kept the same, and the pressure is changed in order to produce supercooled liquids of distinct fragility. The system is the well-known ionic glass-former  $2\text{Ca}(\text{NO}_3)_2 \cdot 3\text{KNO}_3$  (CKN) for which an extensive literature is available on thermodynamic properties, equilibrium structure, and dynamics.<sup>13</sup> In previous MD simulations of CKN,<sup>14</sup> equilibrium structure and dynamics have been investigated as a function of temperature at room pressure. In this work, we simulated CKN at six different pressures, and we obtained the fragility of the supercooled liquids from the temperature dependence of the structural relaxation time and the  $\alpha$  parameter from the temperature dependence of  $F(q,t)$  of the glasses.

The simulated system contained 501 ions (292  $\text{NO}_3^-$ , 83  $\text{Ca}^{2+}$ , and 126  $\text{K}^+$ ) in a cubic box with periodic boundary conditions. The MD simulations were performed with a pairwise additive model given by a Born–Mayer potential energy function.<sup>14,15</sup> In this work, polarization effects on the  $\text{NO}_3^-$  anions were not considered. The nonpolarizable model allows running MD simulations with a time step of 15.0 fs, which is ten times larger than it is possible when using the polarizable model of Ref. 14. Computer time was further saved by handling the long-range electrostatic interactions with the Wolf method<sup>16</sup> instead of the most common Ewald sum method.<sup>17</sup> It has been already shown that both methods give the same thermodynamics, structural, and dynamic properties of CKN.<sup>18,19</sup> Six different pressures were considered:  $10^{-4}$ , 0.5, 1.0, 2.0, 3.0, and 5.0 GPa. For each pressure, the temperature was stepwise reduced from 800 down to 25 K. (In case of pressures of 3.0 and 5.0 GPa, temperatures up to 1000 K were also simulated due to relatively high  $T_g$ .) The same cooling protocol was used for all of the pressures, in which the temperature was reduced in steps of 20 K when close to  $T_g$  and 50 K when far from  $T_g$ . A whole of 176 ( $P, V, T$ ) states were simulated, and for each of them the simulation last for 6.0 ns of equilibration period plus 6.0 ns of production run. Temperature and pressure were controlled by the method of weak coupling to a bath as proposed by Berendsen *et al.*<sup>20</sup> Further computational details can be found in previous publications.<sup>14,18,19</sup>

The glass transition temperature for each pressure  $T_g(P)$  was obtained from plots of density versus temperature  $\rho(T)$ , since  $T_g$  is usually identified in MD simulations as the temperature in which  $\rho(T)$  changes slope. The corresponding curves of the potential energy versus temperature have been also used as a consistency check for the calculation of  $T_g$  at each pressure. The full  $\rho(T)$  dependence has been already discussed in a previous MD investigation of CKN at room pressure,<sup>18</sup> so that here we show the resulting  $T_g$  for the six pressures (black circles in Fig. 1). The  $T_g(P)$  curve obtained from the MD simulations exhibits the same pattern as observed in laboratory for several glass-formers.<sup>21</sup> In fact, the full line in Fig. 1 shows that the empirical expression  $T_g(P) = a(1 + bP)^c$ , where  $a$ ,  $b$ , and  $c$  are adjustable parameters, also holds for the simulation results. Experimental data of  $T_g(P)$  for CKN are available up to 0.2 GPa,<sup>22</sup> which is a much narrower range than investigated in this work. In the low- $P$  limit, the experiment gives  $dT_g/dP \sim 60$  K/GPa.<sup>22</sup>

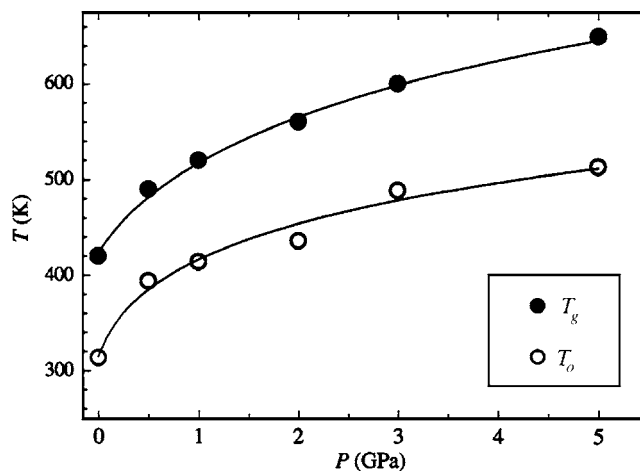


FIG. 1. Pressure dependence of the glass transition temperature of simulated CKN (black circles) and the parameter  $T_0$  of the VFT fit to the temperature dependence of  $\alpha$ -relaxation time (white circles). The full line is the best fit by the empirical equation (Ref. 21)  $T_g(P) = a(1 + bP)^c$ , with  $a = 422$  K,  $b = 2.7$   $\text{GPa}^{-1}$ , and  $c = 0.16$ .

The  $T_g$  values shown in Fig. 1 for the two lowest pressures give a derivative which is *ca.* twice the experimental value. However, the lowest pressure conditions shown in Fig. 1 cover a rather large gap in pressure (0.0001 and 0.5 GPa). In addition, the typical magnitude of pressure fluctuations in a MD simulation is much larger than the average value of 0.0001 GPa in case of the room pressure condition. In fact, further MD simulations of CKN at closer spaced pressures, say 0.5 and 0.3 GPa (not shown), gives  $dT_g/dP \sim 50$  K/GPa, which agrees with experiment. A detailed MD investigation of  $dT_g/dP$  for CKN will be reported in a future publication.

Several quantities related to structural relaxation or transport coefficients, such as diffusion coefficient, viscosity, or ionic conductivity, could be used to calculate the fragility of the CKN model. Since the calculation of the collective intermediate scattering function demands long MD runs, it is usual with the calculation of the self-part,  $F_s(q,t) = \langle \exp[-i\mathbf{q} \cdot (\mathbf{r}_i(t) - \mathbf{r}_i(0))] \rangle$ , by MD simulations along the glass transition range. Structural  $\alpha$ -relaxation time  $\langle \tau_\alpha \rangle$  was obtained from  $F_s(q,t)$  for  $\text{NO}_3^-$  anions in CKN simulated above  $T_g$ . The wave-vector in which  $F_s(q,t)$  was calculated,  $q \sim 2.0$   $\text{\AA}^{-1}$ , corresponds to the main peak of the static structure factor  $S(q)$ . [See Refs. 14 and 18 for a detailed analysis of  $S(q)$  and  $F_s(q,t)$  obtained from MD simulations of CKN at room pressure.] The long-time decay of  $F_s(q,t)$  was fit by a stretched exponential function  $\exp[-(t/\tau)^\beta]$ , from which one obtains the relaxation time as  $\langle \tau_\alpha \rangle = (\tau/\beta) \cdot \Gamma(1/\beta)$ , where  $\Gamma$  is the Euler gamma function. Figure 2 shows  $\langle \tau_\alpha \rangle$  of CKN in an Arrhenius plot with temperature normalized by  $T_g$  for different pressures. Fits by a Vogel–Fulcher–Tammann (VFT) expression,<sup>1</sup>  $\langle \tau_\alpha \rangle = A \exp[B/(T - T_0)]$ , are shown in Fig. 2 as lines on MD data. A first VFT fit to simulation data (bold lines in Fig. 2) suggested that  $\langle \tau_\alpha \rangle$  for the different pressures extrapolate to an average value of  $\sim 10^5$  ns at  $T_g$ . This is a short relaxation time in comparison to  $\sim 100$  s, which usually defines  $T_g$  in real experiments, but is very high for MD simulations. The finding that  $\langle \tau_\alpha \rangle$  extrapolates to a

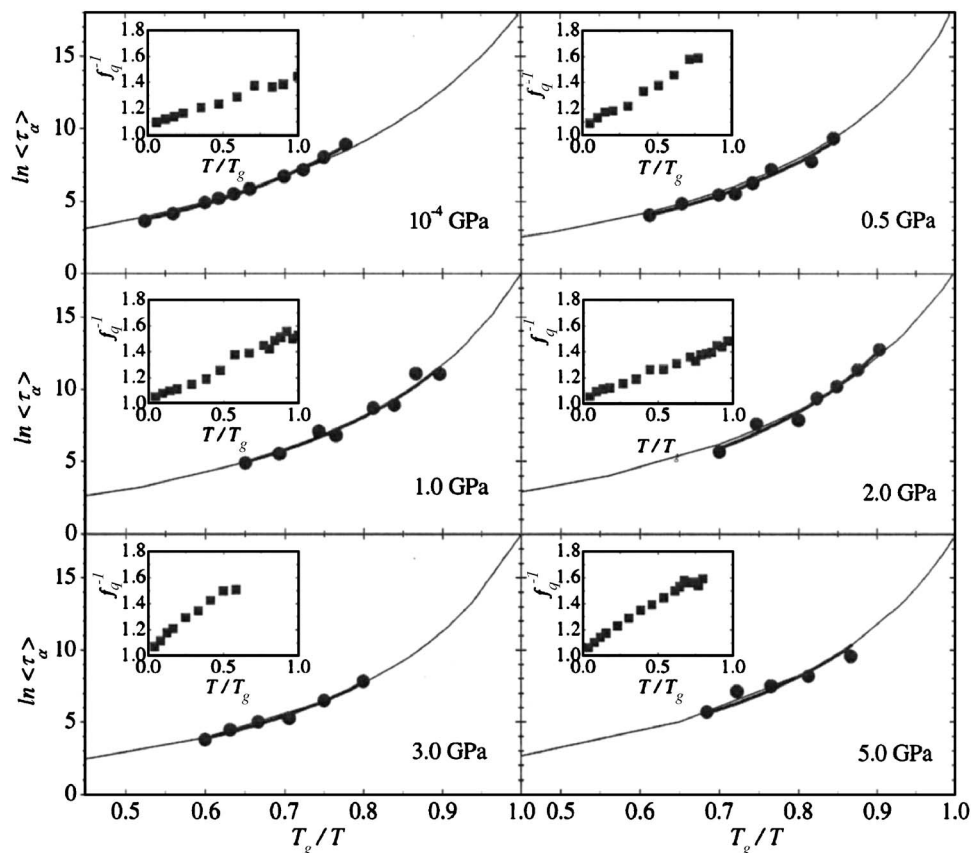


FIG. 2. Structural relaxation time (ps) of CKN at the indicated pressures as a function of the inverse temperature normalized by  $T_g$ . The bold lines are best fit of the VFT equation to MD data. The thin lines show a second VFT fit in which the constraint of identical  $\langle\tau_\alpha\rangle$  at  $T_g$  for all of the pressures has been included in the fit procedure. In each panel, the inset shows the temperature dependence of the inverse of the nonergodicity factor  $f_q^{-1}$  for the corresponding glass.

similar value at  $T_g$  for CKN simulated at different pressures was used in a second fit procedure (thin lines in Fig. 2) in which both the low and the high temperature limits were kept fixed, respectively, at  $10^5$  ns and 1.0 ps. In other words, the VFT fits have the constraint of identical relaxation time at  $T_g$  for all of the pressures. The fragility has been calculated from the VFT parameters  $m = \log(e)BT_g/(T_g - T_0)^2$ .

The resulting parameter  $T_0$  is shown together with  $T_g$  in Fig. 1, in which one sees that both the  $T_g(P)$  and the  $T_0(P)$  curves have similar pressure dependence. In fact, early calorimetric and ionic conductivity measurements of CKN under pressure showed that both the  $dT_g/dP$  and the  $dT_0/dP$  are of similar magnitude.<sup>22,23</sup> It is worth noting that  $T_0$  of CKN simulated at room pressure agrees with the experimental value of 320 K, although the calculated  $T_g$  is significantly higher than the experimental  $T_g = 340$  K.<sup>22,23</sup> The agreement between the values of  $T_0$  obtained by simulation and experiment at variance with those for  $T_g$  is not surprising. Indeed the former is obtained from simulations of well-equilibrated liquid states at high temperature, while the latter are obtained from very high cooling rate in MD simulations, which is known to imply relatively high values of  $T_g$ . Even though liquid fragility has been obtained at the  $T_g$  of the system simulated at each pressure, the actual MD calculation of  $m$  corresponds to low  $\langle\tau_\alpha\rangle$  values in comparison with the experimental definition of glass transition. In other words, the calculation of  $m$  by the MD simulations corresponds to the less steep curvature of the Arrhenius plot at temperatures higher than the experimental  $T_g$ , so that calculated  $m$  is lower than experiment.

The upper inset in Fig. 3 shows  $m$  calculated at different pressures. The MD simulations indicated that the fragility of CKN under pressure is higher than CKN at room pressure. Roland *et al.*<sup>21</sup> collected experimental  $dm/dP$  values for several molecular glass-forming liquids, for which  $m$  usually decreases with increasing pressure, although opposite trends or essentially no pressure dependence of  $m$  are also known (see Table 2 in Ref. 21). In the case of MD simulations of CKN, we have not obtained a smooth trend of  $m$  with pressure; fragility values for the high-pressure simulations are

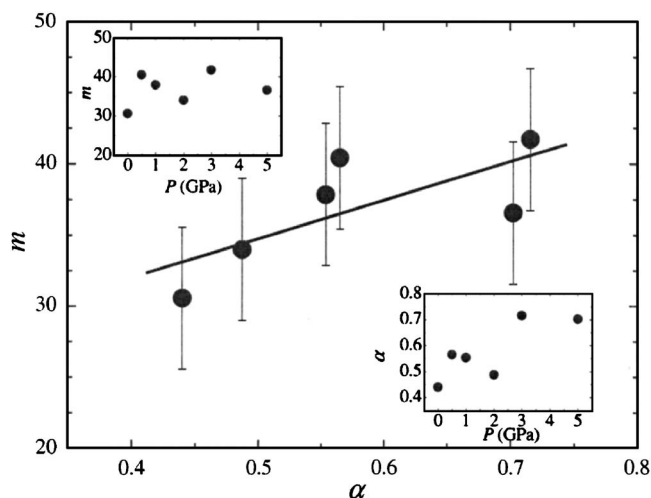


FIG. 3. Correlation between fragility and the nonergodicity  $\alpha$  parameter for CKN simulated at different pressures. The full line is a linear fit to the MD data. The insets give  $m$  and  $\alpha$  values calculated for each pressure.

indeed significantly scattered. Although the simulations at relatively low pressures produced better equilibrated liquid configurations than the simulations at high pressures, the erratic  $m(P)$  behavior cannot be ascribed to the finite equilibration time. We ruled out such possibility performing longer equilibration runs (more than 40.0 ns) at temperatures close to  $T_g$  for the cases of pressures 0.5 and 2.0 GPa. The resulting fragility after this procedure might change by five units, which gives a reasonable estimative of the error on resulting  $m$  (see the error bars in the main Fig. 3). In view of that, we believe that the observed fragility scattering is due the system being trapped in a given single minimum of the potential energy surface upon cooling, so that—in order to perform a correct sampling of the landscape—the cooling procedure should be repeated for several different initial configurations. It is worth noting that one can also find significant deviations on experimental fragility for the same system, for instance, differences of ten units of CKN fragility have been reported by different workers.<sup>24</sup> We stress, however, that the issue here is the correlation between the fragility resulting from a given model for the liquid and the nonergodicity factor of the corresponding glass. With this respect, it is shown below that the scattering of  $m$  for liquid CKN simulated under pressure gives a proportional scattering of  $\alpha$  parameter for the resulting glasses.

The nonergodicity factor  $f_q$  of glassy CKN has been obtained as the plateau reached by the collective intermediate scattering function  $F(q, t)$ , at relatively short time  $t \sim 100.0$  ps. In order to improve the statistics, we considered an average of six wave-vectors in the  $0.25 < q < 0.61 \text{ \AA}^{-1}$  range, which is within the range where the calculated sound velocity shows a linear dispersion with wave-vector.<sup>19</sup> The temperature dependence of  $f_q$  is shown in the insets of Fig. 2 in a  $f_q^-$  vs  $T/T_g$  plot for glassy CKN simulated at six different pressures. It is clear from Fig. 2 that the slope of this plot, which is the  $\alpha$  parameter, changes with pressure.

The  $m$  and  $\alpha$  parameters calculated at each pressure are shown in the insets of Fig. 3, where one sees that the pressure dependence of the liquid fragility is followed by a proportional change of the  $\alpha$  parameter, which carries all of the properties of a harmonic representation of the glassy dynamics. The correlation between  $m$  and  $\alpha$  for the CKN model is given in the main Fig. 3. The MD simulations revealed a linear relation between  $m$  and  $\alpha$  in spite of scattered  $m$  values at high pressures as discussed above, since the  $\alpha$  values are scattered in the same way. It should be noted that the failure between the  $m$  vs  $\alpha$  correlation for CKN suggested in Fig. 7 of Ref. 24 can be assigned to the fact that the  $\alpha$  parameter was estimated from an IXS measurement<sup>25</sup> of CKN in a single temperature of 293 K, whereas the  $\alpha$  parameter is defined by the temperature dependence of  $f_q$  for the glass at low temperature. Therefore, the MD simulations of CKN under pressure confirmed the proposed relationship between long-time structural relaxation of the supercooled liquid and

the short-time vibrational dynamics of the glass.<sup>11</sup> It is our hope that the MD results for CKN will stimulate further measurements as a function of both the temperature and the pressure.

In summary, a model system for the well-known ionic glass-former CKN has been used in a systematic MD investigation of the glass transition at high pressures. The temperature dependence of structural relaxation time changed with pressure, so that we changed the fragility  $m$  of the same model upon the application of pressure. The MD simulations provided a stringent test of the correlation between  $m$  and the vibrational dynamics of the glasses given by the temperature dependence of the nonergodicity factor at low temperature, i.e., the  $\alpha$  parameter. Thus, the MD simulations provided a stringent test on the previously proposed relationship between  $m$  and  $\alpha$ ,<sup>11</sup> and indicated that a change on fragility of the supercooled liquid impinges a signature on the  $\alpha$  parameter of the resulting glass.

The computation facility of CINECA, Italy, is acknowledged. One of the authors (M.C.C.R.) is indebted to FAPESP and CNPq, Brazil, for financial support.

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