Computer simulation study of thermodynamic scaling of dynamics of \(2\text{Ca(NO}_3\text{)}_2 \cdot 3\text{KNO}_3\)

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Molecular dynamics (MD) simulations of the glass-former \(2\text{Ca(NO}_3\text{)}_2 \cdot 3\text{KNO}_3\), CKN, were performed as a function of temperature at pressures 0.1 MPa, 0.5 GPa, 1.0 GPa, and 2.0 GPa. Diffusion coefficient, relaxation time of the intermediate scattering function, and anion reorientational time were obtained as a function of temperature and density \(\rho\). These dynamical properties of CKN scale as \(\rho^\gamma / T\) with a common value \(\gamma = 1.8 \pm 0.1\). The scaling parameter \(\gamma\) is consistent with the exponent of the repulsive part of an effective intermolecular potential for the repulsion between the atoms at shortest distance in the equilibrium structure of liquid CKN, Ca\(^{2+}\), and oxygen atoms of NO\(_3\)\(^-\).

Correlation between potential energy and virial is obeyed for the short-range terms of the potential function, but not for the whole potential including coulombic interactions. Decoupling of diffusion coefficient and reorientational relaxation time from relaxation time take place at a given \(\rho^\gamma / T\) value, i.e., breakdown of Stokes-Einstein and Debye-Stokes-Einstein equations result from combined thermal and volume effects. The MD results agree with correlations proposed between long-time relaxation and short-time dynamics, ln\(\tau\) \(\propto 1/\langle u^2\rangle\), where the mean square displacement \(\langle u^2\rangle\) concerns a time window of 10.0 ps. It has been found that \(\langle u^2\rangle\) scales as \(\rho^\gamma / T\) above and below the glass transition temperature, so that thermodynamic scaling of liquid dynamics can be thought as a consequence of theories relating short- and long-time dynamics, and the more fundamental scaling concerns short-time dynamical properties.


I. INTRODUCTION

The temperature dependence of dynamical properties of glass-forming liquids indicates universal trends followed by many materials in spite of differences in the nature of intermolecular forces.\(^1\) Plots of viscosity, \(\eta\), with \(T\) normalized by the glass-transition temperature \(T_g\), \(\eta\) vs. \(T_g / T\), give the famous classification of supercooled liquids as strong or fragile, as long as \(\eta\) follows or departures, respectively, from the linear Arrhenius dependence at \(T \rightarrow T_g\).\(^2\) More recently, pressure has been addressed as an interesting variable, since thermal and density effects act simultaneously when temperature is changed at fixed room pressure.\(^3\) It is possible to discriminate pure volume effect on transport coefficients of glass-forming liquids by changing pressure. It has been shown that \(\eta\) or structural \(\alpha\)-relaxation time, \(\tau_\alpha\), in a wide range of thermodynamic conditions, overlap on a master curve for a given glass-former when data are plotted as a function of \(\rho^\gamma / T\), where \(\rho\) is density and \(\gamma\) is a characteristic parameter of the system.\(^3\) Writing viscosity as a function \(\mathcal{I}(\rho^\gamma / T)\) provides an interesting collapse of experimental data, although justification based on models is needed for the parameter \(\gamma\) and the actual function \(\mathcal{I}\), which is not the same for different dynamical properties of a given system.

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The scaling parameter \(\gamma\) is related to intermolecular potential \(V(r)\) for a model \(V(r) \propto (1/r)^n\), where \(r\) is the interparticle distance and \(n = 3\gamma\), i.e., a model for which the equilibrium structure of the liquid is determined by an effective repulsive interaction. Scaling of dynamics for some systems has been achieved with \(\gamma \approx 4\), suggesting the connection between \(\gamma\) and the \(n = 12\) repulsive term of the Lennard-Jones potential. However, the parameter \(\gamma\) for different systems covers a wide range, \(0.1 < \gamma < 9.0\).\(^3\) Attempts of tracking trends of \(\gamma\) with the nature of intermolecular potential assign low values of \(\gamma\) to softening of repulsions, for instance, due to flexibility of molecular structure.\(^4, 5\) Low value of \(\gamma\) when scaling the dynamics by \(\rho^\gamma / T\) means enhancement of temperature effect in comparison with volume effect, as one expects in ionic systems with strong intermolecular forces. In case of associated systems with hydrogen bonds, thermodynamic scaling of dynamics is expected to fail if the equilibrium structure of the liquid is modified when temperature and pressure are changed.\(^4, 5\) Thermodynamic interpretation of the parameter \(\gamma\) was given by Casalini et al.,\(^6\) who used the entropy model of Avramov\(^7\) in order to relate \(\gamma\) to heat capacity and thermal expansion coefficient. On the basis of the Avramov model, it has been also proposed the function \(\mathcal{I}(\rho^\gamma / T)\) to fit relaxation times in different conditions of pressure and temperature.\(^6, 8\)

Even though \(\rho^\gamma / T\) scaling of dynamics of glass-forming liquids has been verified for many systems, it is worth noting that molten salts are absent in Table 2 in the review of...
Ref. 3. More recently, thermodynamic scaling has been applied to the so-called ionic liquids, i.e., room-temperature molten salts.9,10 The presence of large asymmetric organic ions in these systems implies interplay between coulombic interactions in polar domains and van der Waals interactions between carbon side chains in non-polar domains that coexist in the equilibrium structure of typical ionic liquids. Depending on the structure of the organic cations and the strength of anion–cation interactions, it has been found γ values ranging from 4.0, like a molecular glass-former with dominance of van der Waals interactions, down to γ ∼ 2.1, indicating smaller role played by volume effects on the ionic liquid dynamics.3,4,11,12 Our understanding on the relationship between the scaling parameter γ and ionic interactions in these complex ionic liquids would improve whether an investigation of thermodynamics scaling was first performed in a more simple molten salt.

In this work, dynamics of the well-known fragile glass-former CKN, 2Ca(NO₃)₂·3KNO₃, is investigated by molecular dynamics (MD) simulations as a function of temperature at four different pressures: 0.1 MPa, 0.5 GPa, 1.0 GPa, and 2.0 GPa. Previous MD simulations of CKN addressed the pressure effect on the fragility,13 and the application of the Ehrenfest equations for dP/dT.14 Here, we take advantage that the potential function is known beforehand, so that MD simulation is an interesting tool to check the relationship between the scaling parameter γ and intermolecular potential. Indeed, systematic MD simulations of Lennard-Jones models with different exponent of the repulsive term (1/r)^n indicated that γ ∼ n/3 is obeyed, or that γ is consistent with an effective (1/r)^m repulsive interaction, m ∼ n, that is, γ ∼ m/3.15,16 Computer simulation has been applied to check thermodynamic scaling of more realistic models, for instance, SiO₂,17 although silica is the archetypical strong liquid for which fail of thermodynamic scaling is expected due to changes on the network under high pressure. Computer simulation has also been used to investigate thermodynamic scaling in an ionic liquid,18 namely, 1-ethyl-3-methylimidazolium nitrate, for which γ ∼ 4 has been obtained from ionic diffusion coefficients.

In this work, thermodynamic scaling of CKN dynamics is checked for diffusion coefficients, and relaxation times obtained from the intermediate scattering function and reorientational correlation function of nitrate anions. In Sec. III A, it is shown that these dynamical properties scale as ργ/T, with a common value γ ∼ 1.8, which is relatively small in comparison with molecular glass-formers with dominance of van der Waals interactions, but is reasonable in light of strong coulombic forces in a molten salt that reduce the role played by volume in comparison with temperature effect on the liquid dynamics. In Sec. III B, we argue that γ ∼ 1.8 is consistent with the slope at short-range distance of an effective repulsive intermolecular potential, reminding that the species in closest approach in CKN are Ca²⁺ and the oxygen atoms of NO₃⁻. It is also discussed the relationship between thermodynamic scaling with proposed correlation of fluctuations between potential energy and virial that holds for a potential model of the form (1/r)^γ.16 Breakdown of the Stokes-Einstein and the Debye-Stokes-Einstein equations,3,19,20 relating structural relaxation time with, respectively, diffusion coefficient and reorientational time, are observed at different temperatures for CKN simulated at each pressure. However, it is discussed in Sec. III C that these decoupling phenomena scale as ργ/T, i.e., decoupling should not be assigned exclusively to a given temperature above T_g, instead decoupling is due to combined thermal and volume effects. Finally, in contrast to the famous Vogel-Fulcher-Tamman-Hesse equation with divergent viscosity at T_o below T_g, the finding that the function 3(ργ/T)^2 has no singularity is discussed in light of some formulas that also have no divergence. In Sec. III D, it is shown that the universal scaling of relaxation time by the mean squared displacement at short time, 1<T<1/(u²), valid for many glass-formers,21-23 also applies for CKN simulated at different thermodynamic states. Consequently, 1/(u²) scales as ργ/T, even though (u²) is calculated within the short time range of 10.0 ps, whereas γ was previously obtained from long time relaxation and diffusive processes. In other words, if such a theory based on the interesting connection between short- and long-time dynamics is correct, ργ/T scaling of relaxation times is a consequence of ργ/T scaling of short time dynamics.

II. COMPUTATIONAL DETAILS

The MD simulations of CKN were performed with a non-polarizable pairwise potential given by a Born-Mayer function:

\[
V(\mathbf{r}_{\alpha i \beta j}) = \sum_{\alpha i = 1}^{N-1} \sum_{\beta j = 1}^{m} \sum_{\alpha \neq \beta} \sum_{i \neq j} A_{\alpha \beta} e^{-B_{\alpha \beta} / r_{\alpha i \beta j}} - \frac{C_{\alpha \beta}}{r_{\alpha i \beta j}^6} + \frac{q_{\alpha} q_{\beta}}{r_{\alpha i \beta j}^2},
\]

(1)

where r_{\alpha i \beta j} is the distance between atom \alpha of ion i and atom \beta of ion j, the number of sites m is four for NO₃⁻ and one for Ca²⁺ and K⁺, and cations carry their full formal charges. We used the parameters of Signorini et al.24 for A_{\alpha \beta}, B_{\alpha \beta}, C_{\alpha \beta}, and partial charges q_{\alpha} of NO₃⁻ (see Table I of Ref. 24). The number of ions N was 501 in a cubic box, i.e., 292 NO₃⁻, 83 Ca²⁺, and 126 K⁺. Temperature was reduced from 800 K in steps of 50 K, and steps of 20 K when close to T_g, down to 100 K. Each cooling procedure was performed at pressures 0.1 MPa, 0.5 GPa, 1.0 GPa, and 2.0 GPa. Temperature and pressure were controlled by the method of Berendsen et al.25 Simulation runs lasted of 12 ns with time step of 15 fs were performed for each (P, V, T) state. Long-range electrostatic interactions were handled with the Wolf method,26 instead of the most common Ewald sum method,27 in order to reduce computer time. It has been already shown that both methods give the same thermodynamic, structural, and dynamic properties of CKN.28 The nitrate anion was considered as a rigid body, a quaternion approach was used for rotational dynamics, and the equations of motion were solved with leapfrog algorithms.27
III. RESULTS AND DISCUSSION

A. The scaling parameter \( \gamma \)

Figure 1 shows the temperature dependence of density of CKN simulated at different pressures, and the glass transition temperature \( T_g \) is the temperature where \( \rho(T) \) changes the slope. It has been already shown in Ref. 13 that the pressure dependence \( T_g(P) \) obtained from the MD simulations follows the usual empirical equation,

\[
T_g(P) = A (1 + bP)^c
\]

where \( a, b, \) and \( c \) are adjustable parameters. However, it is worth remembering that very fast cooling rate in MD simulations implies \( T_g \) higher than experiment (the experimental \( T_g \) of CKN is 335 K, and \( dT_g/dP = 60 \) K/GPa, at room pressure).29 Accordingly, it was estimated that the simulated system departs from equilibrium when relaxation times reach \( \sim 10^5 \) ns,13 which is a long time for MD simulations, but much smaller than usually considered in experiments (\( \sim 10^2 \) s). Nevertheless, thermodynamic scaling of liquid dynamics implies that \( \rho/T \) should be the same for \( T_g \) and \( \rho(T_g) \) at different pressures if the glass transition corresponds to a given value of relaxation time. In fact, Table I shows that \( \rho(T_g) \) of Fig. 1 result in approximately the same \( \rho/T \) ratio, where \( \gamma = 1.8 \) has been not determined from these few \( \rho(T_g(P)) \) values, instead \( \gamma \) was obtained from relaxation times above \( T_g \) as discussed in the following.

Computer simulations allow the investigation of a wide range of \( \rho \) and \( T \), but the calculation of a collective time correlation function, such as the stress tensor correlation function needed for viscosity, is difficult at high pressure proper to very slow dynamics. In a previous work,13 we related the non-ergodic factor of glassy CKN with the relaxation time of liquid CKN obtained from the incoherent scattering function, 

\[
F_i(k, t) = \langle \exp\{-ik \cdot (\mathbf{r}_i(t) - \mathbf{r}_i(0))\} \rangle,
\]

where \( \mathbf{r}_i(t) \) is the coordinate of ion \( i \) at time \( t \), calculated at \( t \sim 2.0 \, \text{ Å}^{-1} \), i.e., the wave vector corresponding to the main peak of the static structure factor \( S(k) \). The \( F_i(k, t) \) was fit by stretched exponential function, \( \exp\{-t/\tau_\alpha^\beta\} \), in order to obtain the relaxation time \( \tau_\alpha \), where \( \Gamma \) is the Euler gamma function. The wide range of \( \tau_\alpha \) values for anions can be seen in the inset of Fig. 2 as an Arrhenius plot for each pressure. The main Fig. 2 shows that these data overlap when plotted as a function of \( \rho/T \), with the \( \rho(T, P) \) values of Fig. 1, and the best fit scaling parameter \( \gamma = 1.8 \pm 0.1 \). Recently, Fragiadakis and Roland30 pointed out that \( \rho/T \) scaling actually concerns reduced quantities, for instance, \( \tau_\alpha = v^{-1/3}(kT/m)^{1/2} \tau_\alpha \), where \( v \) is molecular volume, \( m \) is molecular mass, and \( k \) is the Boltzmann constant. Considering reduced quantities, rather than the raw data, is important when testing thermodynamic scaling of dynamics within the normal liquid regime. However, in case of the CKN data of Fig. 2, the difference between \( \tau_\alpha \) and \( \tau_\alpha \) is not important because relaxation time or viscosity in the supercooled liquid regime changes by orders of magnitude within a few percent of changing in density and temperature.30

After obtaining \( \gamma = 1.8 \) from scaling of \( \tau_\alpha \), we checked whether the same parameter would be able to scale other dynamical properties of CKN. Relaxation time for reorientation of anions was obtained from the correlation function \( C_r(t) = \langle \mathbf{u}_i(t) \cdot \mathbf{u}_i(0) \rangle \), where \( \mathbf{u}_i \) is an unitary vector on the \( C_3 \) axis of \( NO_3^- \). Reorientational relaxation time \( \tau_r \) was obtained as the time that the normalized \( C_r(t) \) decreases by 1/e from the initial value. Inset of Fig. 3 shows Arrhenius plot of \( T_\tau \) because of the relationship to viscosity according to the Debye-Stokes-Einstein equation, \( T_\tau \propto \eta \). The main part of Fig. 3 shows that good overlap of data is achieved when \( T_\tau \) is plotted as a function of \( \rho/T \) with \( \gamma = 1.8 \). Diffusion coefficient, \( D \), was obtained from the linear regime at long time of the mean squared displacement, MSD, \( \langle |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \rangle \). Inset of Fig. 4 shows Arrhenius plot of \( T/D \) for anions because of the relationship to viscosity according to the

![Figure 1](https://example.com/figure1.png)

**FIG. 1.** Temperature dependence of density of CKN simulated at 0.1 MPa (black circles), 0.5 GPa (red circles), 1.0 GPa (green circles), and 2.0 GPa (blue circles). Full lines are linear fits to low and high temperature data, whose intercepts indicated by squares connected by lines give the pressure dependence of the glass transition temperature, \( T_g(P) \).

![Figure 2](https://example.com/figure2.png)

**FIG. 2.** Relaxation time of the incoherent intermediate scattering function of anions in a plot scaled by \( \rho/T \) with \( \gamma = 1.8 \) for CKN simulated at 0.1 MPa (black circles), 0.5 GPa (red circles), 1.0 GPa (green circles), and 2.0 GPa (blue circles). Full line is the fit by Eq. (2) with \( A = 30.2 \) ps, \( B = 202.5 \), and \( C = 4.3 \). Inset shows the same data in an Arrhenius plot for each pressure.

### Table I. Glass-transition temperature, \( T_g \), and density at \( T_g \) calculated by MD simulations of CKN at different pressures. Corresponding \( \rho/T \) values are shown with \( \gamma = 1.8 \).

<table>
<thead>
<tr>
<th>( P ) (GPa)</th>
<th>( T_g ) (K)</th>
<th>( \rho ) (g·cm(^{-3}))</th>
<th>( \rho/T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-4} )</td>
<td>406</td>
<td>2.239</td>
<td>0.011</td>
</tr>
<tr>
<td>0.5</td>
<td>497</td>
<td>2.300</td>
<td>0.009</td>
</tr>
<tr>
<td>1.0</td>
<td>533</td>
<td>2.392</td>
<td>0.009</td>
</tr>
<tr>
<td>2.0</td>
<td>542</td>
<td>2.515</td>
<td>0.010</td>
</tr>
</tbody>
</table>
Stokes-Einstein equation, $T/D \propto \eta$. The main part of Fig. 4 shows that good overlap of data is achieved when $T/D$ is plotted as a function of $\gamma$. Previous MD simulations of CKN showed that ionic mobility of NO$_3^-$ is similar to K$^+$, and significantly higher than Ca$^{2+}$. Thermodynamic scaling of CKN dynamics was also found for the other species, for instance, Fig. 5 shows reasonable scaling of the corresponding $T/D$ data for Ca$^{2+}$.

The collapse of data in Figs 2–5 with the same $\gamma$ does not depend on any assumed function $\Im(\rho/T)$. After obtaining $\gamma$, these data were fit by the function,

$$\Im\left(\frac{\rho}{T}\right) = A \exp\left(B \frac{\rho^\gamma}{T}\right)^C,$$

where $A$, $B$, and $C$ are adjustable parameters. This form of $\Im(\rho/T)$ has been justified by Casalini et al. on the basis of the entropy model of Avramov. It is a characteristic feature of thermodynamic scaling of liquid dynamics that the same scaling parameter $\gamma$ is valid for different properties, even though the actual function $\Im(\rho/T)$ might be different for each property, as indicated by distinct parameters given in the captions of Figs. 2–5. The finding of equal parameter $\gamma$, but different function $\Im$ for different properties, has been explained by the Ngai’s coupling model. In the coupling model, the stretched exponent $\beta$ of a time correlation function decaying like $\exp[−(t/\tau)^\beta]$ is interpreted as $\beta \equiv 1−n$, where larger coupling parameter $n$ implies more stretched relaxation, i.e., $n$ is an effective measurement of dynamical cooperativity. The stretched exponential decay starts after a short-time period in which the relaxation is still exponential, $\exp[−(t/\tau_o)]$. It turns out from the crossover between these two regimes that the $\alpha$-relaxation time $\tau_a$ depends on the primitive relaxation time $\tau_o$ and the coupling parameter $n$. Bearing in mind that different dynamical properties decay as $\exp[−(t/\tau)^n]$ with distinct $n$, the actual function $\Im(\rho/T)$ is also different for each property. It should be noted that according to the coupling model the $\rho/T$ scaling of viscosity or $\tau_a$ is already a consequence of a more fundamental $\rho/T$ scaling of $\tau_o$. This is analogous to the idea discussed in Sec. III D, where we show thermodynamic scaling of a short-time dynamical property, namely, the ionic mean squared displacement.

In a previous work, we calculated several thermodynamic properties of CKN in order to test the application of the Ehrenfest relations for the pressure dependence of $T_g$. It was found that the equation $dT_g/dP = TV\Delta\kappa_T/\Delta\alpha_P$ was not obeyed, whereas $dT_g/dP = TV\Delta\alpha_P/\Delta C_P$ was obeyed, where $\alpha_P$ is the isobaric thermal expansivity, $\kappa_T$ is the isothermal compressibility, $C_P$ is the isobaric heat capacity, and $\Delta$ means the difference between liquid and glass values of a given property, $\Delta X = X(\text{liquid}) − X(\text{glass})$. The finding that $dT_g/dP$ does not follow the first of the Ehrenfest equations, while $dT_g/dP$ follows the second equation, is usually assigned as an indication that excess volume is not the parameter which determines the glass transition, rather entropy or enthalpy determines the glass transition. In spite of lively debates on the interpretation of the Ehrenfest equations for $dT_g/dP$, this work is in line with the previous study on the application of Ehrenfest equations for CKN, since scaling of the CKN dynamics by $\rho/T$ with a relatively small value of $\gamma$ means dominance of thermal over volume effect on dynamics.

The calculation of these thermodynamic properties allows further consistency tests on the scaling parameter $\gamma$ of

![Figure 3](image3.png)

**FIG. 3.** The product of temperature and reorientational relaxation time of NO$_3^-$ in a plot scaled by $\rho/T$ with $\gamma = 1.8$ for CKN simulated at 0.1 MPa (black circles), 0.5 GPa (red circles), 1.0 GPa (green circles), and 2.0 GPa (blue circles). Full line is the fit by Eq. (2) with $A = 402.2$ K ps, $B = 408.5$, and $C = 1.4$. Inset shows the same data in an Arrhenius plot for each pressure.

![Figure 4](image4.png)

**FIG. 4.** The quotient of temperature by diffusion coefficient of NO$_3^-$ in a plot scaled by $\rho/T$ with $\gamma = 1.8$ for CKN simulated at 0.1 MPa (black circles), 0.5 GPa (red circles), 1.0 GPa (green circles), and 2.0 GPa (blue circles). Full line is the fit by Eq. (2) with $A = 584.4$ K $10^{-8}$ m$^2$ s$^{-1}$, $B = 487.1$, and $C = 1.6$. Inset shows the same data in an Arrhenius plot for each pressure.

![Figure 5](image5.png)

**FIG. 5.** The same as Figure 4, but for Ca$^{2+}$ cations. The fit by Eq. (2) was achieved with $A = 314.8$ K $10^{-8}$ m$^2$ s$^{-1}$, $B = 750.6$, and $C = 1.4$. 
dynamics of liquid CKN. Pensado et al. \textsuperscript{11} obtained a relationship between the pressure and temperature dependences of viscosity, which in terms of relaxation time is

\begin{equation}
\frac{\partial \tau_\alpha}{\partial P} = - \gamma \left( \frac{1}{\gamma T} + \alpha_P \right) \frac{\partial \tau_\alpha}{\partial T}.
\end{equation}

We estimated the derivatives \((\partial \tau_\alpha/\partial P)_T\) and \((\partial \tau_\alpha/\partial T)_P\) by finite differences for some pairs of thermodynamic states, and by using \(\alpha_P\) and \(\gamma_T\) calculated from the MD simulations, we tested Eq. (3) with the value \(\gamma = 1.8\). For instance, consider the following data for CKN: \(\tau_\alpha(800 \text{ K}, 0.5 \text{ GPa}) = 71 \text{ ps}, \tau_\alpha(750 \text{ K}, 0.5 \text{ GPa}) = 137 \text{ ps}, \tau_\alpha(800 \text{ K}, 1.0 \text{ GPa}) = 134 \text{ ps}, \) and \(\tau_\alpha(750 \text{ K}, 1.0 \text{ GPa}) = 247 \text{ ps}\). We estimate the averages at the middle point 775 K and 0.75 GPa, \((\partial \tau_\alpha/\partial P)_T = 173 \text{ ps/GPa}, \) and \((\partial \tau_\alpha/\partial T)_P = -1.8 \text{ ps/K}\). The corresponding densities are: \(\rho(800 \text{ K}, 0.5 \text{ GPa}) = 2.161 \text{ g/cm}^3, \rho(750 \text{ K}, 0.5 \text{ GPa}) = 2.180 \text{ g/cm}^3, \rho(800 \text{ K}, 1.0 \text{ GPa}) = 2.264 \text{ g/cm}^3,\) and \(\rho(750 \text{ K}, 1.0 \text{ GPa}) = 2.282 \text{ g/cm}^3\). Thus, we estimate the averages at the middle point 775 K and 0.75 GPa, \(\alpha_P = 1.635 \times 10^{-4} \text{ K}^{-1}\), and \(\gamma_T = 0.0924 \text{ GPa}^{-1}\). Therefore, the right hand side of Eq. (3) gives 188 ps/GPa, which is close to the actual value \((\partial \tau_\alpha/\partial P)_T = 173 \text{ ps/GPa}\). It is worth noting that, following Ref. 11, Eq. (3) accounts for the relationship between \((\partial \tau_\alpha/\partial P)_T\) and \((\partial \tau_\alpha/\partial T)_P\) as long as the term \(1/\gamma T\) is included. Previous work\textsuperscript{33} gave a similar equation without the term 1/\(\gamma T\) by assuming that free volume was the only factor determining viscosity. Since the relatively small \(\gamma\) for CKN implies dominance of thermal effects, it is reasonable that the full Eq. (3) is needed. Another way to put forward the relative importance of volume and temperature effects on relaxation time is the ratio of activation energies at isochoric and isobaric conditions, \(E_V/E_P\).\textsuperscript{11} The range \(0 < E_V/E_P < 1\) means that \(E_V/E_P = 1\) if \(\tau_\alpha\) depends only on \(T\), while \(E_V/E_P \ll 1\) is more important as the volume effect. In terms of the scaling parameter, this ratio is given by \(E_V/E_P = (1 + \gamma T \alpha_P)^{-1}\).\textsuperscript{11} The value \(\alpha_P = 1.635 \times 10^{-4} \text{ K}^{-1}\) estimated for CKN at 775 K and 0.75 GPa implies \(E_V/E_P = 0.81\), which is larger than ratios for several molecular glass-formers and room temperature molten salts (see Table 1 in Ref. 11) because of dominance of temperature over volume effect on the CKN dynamics.

**B. Relationship of \(\gamma\) to intermolecular potential**

The value \(\gamma = 1.8\) obtained from the MD simulations of CKN is reasonable in light of experimental investigations of thermodynamic scaling of dynamics of ionic liquids based on complex organic ions such as imidazolium cations.\textsuperscript{4,5,11,12,18} Low values of \(\gamma\) in ionic liquids was assigned to strong interactions when small size anions are considered with a given cation. The smallest \(\gamma\) was reported for 1-octyl-3-methylimidazolium tetrafluoroborate, \(\gamma = 2.2\),\textsuperscript{5} which is still larger than the value obtained here for CKN. In MD simulations of an ionic liquid based on the same anion as this work, namely, 1-ethyl-3-methylimidazolium nitrate,\textsuperscript{18} it has been found \(\gamma = 4.0\). Therefore, \(\gamma = 1.8\) seems reasonable for CKN proper to stronger ionic interactions in CKN in comparison with these organic molten salts.

In case of a system with three different ions, it is not immediately clear which of the repulsive interactions should be related to the scaling parameter \(\gamma\). We agree with the authors of Ref. 18 that the relationship between \(\gamma\) and intermolecular potential should be found in the anion–cation repulsion. Partial radial distribution functions, \(g_{\text{CaO}}(r)\), calculated by MD simulations of CKN indicate that the species in closest approach are Ca\textsuperscript{2+} and oxygen atoms of NO\textsubscript{3}\textsuperscript{−}.\textsuperscript{28} Figure 6 shows the potential energy function, Eq. (1), for Ca–O interaction, and for comparison purpose \(g_{\text{CaO}}(r)\) calculated by MD simulation of CKN. It is shown in Fig. 6 that \(V(r)\) of Ca–O interaction can be represented by a sum of \(r^{-1}\) long-range attraction due to coulombic interaction, and \(r^{-n}\) repulsion at short distance. The best fit to \(V(r)\) shown in Fig. 6 gives the repulsive exponent \(n = 4.7\), so that \(n/3 = 1.5\) is in fact close to \(\gamma = 1.8\) obtained from thermodynamic scaling of CKN dynamics.

Another consequence of an effective inverse power law for the intermolecular potential is the correlation between pressure and energy discussed at length by Bailey et al.\textsuperscript{16} Computer simulations showed that the potential energy and the configurational part of the virial function might be strongly correlated to each other along the steps of a MD simulation. Strongly correlated systems can be made of more than one kind of particle, but pressure–energy correlation is destroyed when \(r^{-n}\) and \(r^{-m}\) terms with different ranges \(n\) and \(m\) are simultaneously present in the potential function.\textsuperscript{16} This is the case of a molten salt with repulsive short-range and coulombic interactions. Recently, weak pressure–energy correlation has been discussed for CKN,\textsuperscript{33} and the top panel of Fig. 7 shows in fact no pressure–energy correlation for CKN. However, if one calculates separately the short-range interactions (the first two terms in Eq. (1)) and the long-range coulombic interactions (the third term in Eq. (1)), then pressure–energy correlation is observed for CKN (middle and bottom panels of Fig. 7). Pressure–energy correlation is particularly well obeyed for the short-range interactions in CKN. In case of an intermolecular potential given by an inverse power law \(r^{-n}\), this correlation would be exact and the slope

![Image](https://example.com/image.png)
of this plot would be \( \gamma = nT^3 \).\textsuperscript{16} Data in Fig. 7 have been shown as fluctuation about the average value for comparison purpose, but if one considers energy and virial in units of kJ/mol, the linear fit in the middle panel of Fig. 7 is achieved with slope 1.84, which agrees with the scaling parameter of CKN dynamics.

C. Breakdown of Stokes-Einstein and Debye-Stokes-Einstein equations

The temperature dependence of diffusion coefficient \( D \) and reorientational time \( \tau_r \) follows the \( \alpha \)-relaxation time \( \tau_\alpha \) at high temperature according to the Stokes-Einstein (SE) and Debye-Stokes-Einstein (DSE) equations, but departures from \( \tau_\alpha \) for supercooled liquids at temperatures below \( \sim 1.3 T_g \).\textsuperscript{19,20} Considering NO\(_3^−\) dynamics in CKN, the upper insets in Figs. 8 and 9 show that \( D\tau_\alpha/T \) and \( \tau_\alpha/(\tau_\rho T) \) increase for \( T \) below a temperature that is higher as higher is the pressure because \( T_g \) increases with pressure. However, the temperature where these ratios depart from a constant value is not simply related to \( T_g(P) \), i.e., breakdown of SE and DSE equations for CKN does not take place at the same temperature reduced by \( T_g \). Another way to report deviation from SE and DSE equations is the proposition of fractional dependences, \( D/T \propto \tau_\alpha^\xi \) and \( T \tau_\rho \propto \tau_\alpha^\zeta \). The bottom insets in Figs. 8 and 9 show that fractional SE and DSE equations are followed for NO\(_3^−\) dynamics in CKN. The collapse of CKN data to a single curve is in line with experimental data of different liquids under high pressures,\textsuperscript{20} and the finding \( \xi < \zeta \) has been also observed for other glass-forming liquids.\textsuperscript{34,35} The exponent \( \xi = 0.70 \) accounts for the temperature and pressure dependence of NO\(_3^−\) diffusion coefficient, but reorientational relaxation exhibits two regimes with \( \xi = 0.50 \) and \( \zeta = 0.24 \) for small and long \( \alpha \)-relaxation times, respectively.

Since each of the dynamical property \( \tau_\alpha, D, \) and \( \tau_r \) for NO\(_3^−\) in liquid CKN follows thermodynamic scaling, it is

\[ \frac{D\tau_\alpha}{T} \propto \frac{\tau_\alpha}{T^\xi} \]

FIG. 8. The \( D\tau_\alpha/T \) ratio for NO\(_3^−\) as a function of \( \rho/T \) with \( \gamma = 1.8 \) for CKN simulated at 0.1 MPa (black circles), 0.5 GPa (red circles), 1.0 GPa (green circles), and 2.0 GPa (blue circles). The upper inset shows the same data as a function of temperature, indicating that decoupling starts at different temperature for each pressure. In the bottom inset, the full line indicates the fractional Stokes-Einstein equation, \( D/T \propto (\tau_\alpha)^\xi \), with \( \xi = -0.70 \).

FIG. 9. The \( \tau_\alpha/\tau_r T \) ratio for NO\(_3^−\) as a function of \( \rho/T \) plot with \( \gamma = 1.8 \) for CKN simulated at 0.1 MPa (black circles), 0.5 GPa (red circles), 1.0 GPa (green circles), and 2.0 GPa (blue circles). The upper inset shows the same data as a function of temperature, indicating that decoupling starts at different temperature for each pressure. In the bottom inset, the full lines indicate that fractional Debye-Stokes-Einstein equation, \( \tau_\alpha T \propto (\tau_\rho)^\zeta \), is obeyed with distinct exponent \( \xi \) at low and high temperature, respectively, 0.50 and 0.24.
reasonable to ask whether the breakdown of SE and DSE equations also scale as \( \rho^2/T \). The main Figs. 8 and 9 show \((D\tau_o)/T\) and \(\tau_o/\langle u \rangle\) as functions of \(\rho^2/T\), with the previously obtained parameter \(\gamma = 1.8\). In fact, breakdown of SE and DSE equations obey thermodynamic scaling. Breakdown of SE and DSE equations in supercooled liquids is usually interpreted as a result of dynamical heterogeneity,\textsuperscript{19, 20, 34, 35} as immobile particles following the SE and DSE equations coexist with regions of relatively mobile particles. However, fractional equations have been observed for normal liquids at temperatures above the supercooled regime,\textsuperscript{20} and MD simulations indicated breakdown of SE and DSE equations for both the groups of immobile and mobile molecules.\textsuperscript{34, 35} The explanation according to the Ngai’s coupling model\textsuperscript{19, 32} follows similar reasoning as considered in Sec. III A concerning different \(\langle \rho^2/T \rangle\) functions for each dynamical property. The primitive relaxation time \(\tau_o\) has the same temperature dependence irrespective of the dynamical property, since the coupling model considers \(\tau_o\) as the relaxation time of the exponential decay before many-body relaxation sets in. However, different properties exhibit different temperature dependence because each one weighs the many-body relaxation in different way, since the stretch exponent \(\beta\) of the corresponding time correlation function is given by the coupling parameter \(n, \beta \equiv 1-n\). The coupling model interpretation seems more reasonable than the picture of dynamical heterogeneity to explain thermodynamic scaling of the breakdown of SE and DSE equations for CKN. It is worth stressing that this statement does not diminish the importance of dynamics heterogeneity in glass-forming liquids, including CKN since previous MD simulations have already discussed heterogeneity in this system.\textsuperscript{36} On the other hand, the coupling model explanation seems more consistent with the finding that the breakdown of SE and DSE equations for CKN starts at a combined value of density and temperature according to \(\rho^2/T\) scaling.

D. Thermodynamic scaling of short-time mean squared displacement

The finding that the temperature dependence of viscosity or relaxation time of supercooled liquids departs from Arrhenius behaviour can be rephrased in terms of an activation energy \(E_o\) that is not a constant, instead \(E_o(T)\) is a temperature dependent property. Different theories or models assign \(E_o(T)\) to different properties, for instance, thermodynamic theories in which \(E_o(T)\) is inversely proportional to configurational entropy\textsuperscript{37} or free volume,\textsuperscript{38} and elastic models\textsuperscript{39} in which the temperature dependence \(E_o(T)\) comes from short-time dynamical properties, such as high-frequency sound velocity \(c_\infty\), high-frequency shear modulus \(G_\infty\), and short-time mean squared displacement \(\langle u^2 \rangle\). These short-time (high-frequency) dynamical properties are related to each other in case of a simple one-dimensional harmonic model, and they change continuously with temperature exhibiting different single slopes at high and low temperatures.\textsuperscript{39} Therefore, like the concept of \(\rho^2/T\) scaling of dynamics, in these elastic models no divergence of viscosity comes into scene at \(T_g\) or any temperature below \(T_g\). Whether models that explicitly connect long- and short-time dynamics are correct, one expects that \(\rho^2/T\) scaling would be already a consequence of \(\rho^2/T\) scaling of a short-time dynamical property.

Universal scaling of relaxation dynamics has been found for many glass-formers when \(E_o(T)\) is related to the mean squared displacement.\textsuperscript{21–23} In this work, we consider the simple relationship \(\tau_o \propto \exp(C/\langle u^2 \rangle)\), where \(C\) is a constant, and it is supposed that \(\langle u^2 \rangle\) is obtained or calculated within the picosecond range. Recently, universal scaling by short-time vibrational dynamics was shown valid for CKN,\textsuperscript{23} where \(\langle u^2 \rangle\) was measured at 10 ps by inelastic neutron scattering spectroscopy.\textsuperscript{40} Therefore, we obtained \(\langle u^2 \rangle\) at 10 ps as a function of temperature for each species in CKN simulated at each pressure. Amplitudes \(\langle u^2 \rangle\) for NO3\textsuperscript{−} and K\textsuperscript{+} are similar, whereas \(\langle u^2 \rangle\) for Ca\textsuperscript{2+} is significantly smaller, and Fig. 10 illustrates the temperature dependence of \(\langle u^2 \rangle\) for NO3\textsuperscript{−} and Ca\textsuperscript{2+} calculated by MD simulations of CKN. Experimental results at room pressure obtained by inelastic neutron scattering spectroscopy were shown by Kartini et al.\textsuperscript{40} as the difference \(\langle u^2 \rangle(T) - \langle u^2 \rangle(T = 300K)\). For comparison purpose, data provided in Fig. 7 of Ref. 40 are shown in the inset of Fig. 10 together with \(\langle u^2 \rangle\) for NO3\textsuperscript{−} and Ca\textsuperscript{2+} calculated by MD simulations at room pressure. The magnitude of \(\langle u^2 \rangle\) calculated in this work is reasonable in comparison with the neutron scattering results. In line with experimental data for several glass-formers, Fig. 10 indicates that the steeper high temperature regime of \(\langle u^2 \rangle\) does not necessarily start exactly at \(T_g\). When attempting to relate \(\langle u^2 \rangle\) and \(\tau_o\) in a three species system like CKN, it is not immediately obvious whether \(\langle u^2 \rangle\) should be a sum or average of values for each species. Nevertheless, Fig. 11 shows \(\tau_o\) as a function
FIG. 11. Relaxation time of the incoherent scattering function for NO$_3^-$ as a function of reciprocal of the corresponding short-time mean squared displacement of CKN simulated at 0.1 MPa (black circles), 0.5 GPa (red circles), 1.0 GPa (green circles), and 2.0 GPa (blue circles). Full line is a linear fit to the data.

of the reciprocal of $\langle u^2 \rangle$ for the anion, which is the more mobile species in CKN. In comparison with the Arrhenius plot of $\tau_\alpha$ shown in the inset of Fig. 2, there is a remarkable collapse of $\tau_\alpha$ data when plotted in terms of reciprocal $\langle u^2 \rangle$.

It should be noted that the logarithm plot of $\tau_\alpha$ as a function of $1/\langle u^2 \rangle$ in Fig. 11 corresponds to MD results for CKN above $T_g$ for each pressure. As shown in Fig. 10, $\langle u^2 \rangle$ is easily calculated by MD simulations within the whole temperature range since $\langle u^2 \rangle$ is a short-time property. The $\langle u^2 \rangle$ data for NO$_3^-$ and Ca$^{2+}$ of Fig. 10 are plotted again in Fig. 12 as a function of $\rho\gamma/T$ of CKN dynamics is obeyed in spite of CKN is not a strong correlated system. In fact, dropping the coulombic terms in the calculation of potential and virial, and considering only the short-range contributions, then strong potential energy–virial correlation is observed, and it is consistent with $\gamma = 1.8$. The value of $\gamma$ for molten CKN is smaller than recently reported for room temperature ionic liquids, indicating smaller volume effect, or larger temperature effect on dynamics due to stronger interactions in CKN than in ionic liquids. The MD simulations showed that diffusion coefficient and reorientational relaxation of NO$_3^-$ departure from the temperature dependence of $\alpha$-relaxation time at a given temperature above $T_g$. The breakdown of Stokes-Einstein and Debye-Stokes-Einstein is a well-known experimental fact, but the MD simulations of molten CKN showed that such breakdown also follows $\rho\gamma/T$ scaling, so that decoupling of these dynamical properties is an effect resulting from combined volume and temperature effects. Finally, we considered an example of models relating short- and long-time dynamics of supercooled liquids, that is, a model in which activation energy for viscosity or $\alpha$-relaxation time depends on the short-time mean squared displacement. We found that $\langle u^2 \rangle$ calculated for CKN scales as $\rho\gamma/T$, so that thermodynamic scaling of relaxation dynamics can be interpreted in these theories as the consequence of scaling of short-time dynamics. It would be interesting to pursue experimental confirmation by high pressures measurements of different liquids whether thermodynamic scaling holds for $\langle u^2 \rangle$. It would be also interesting to check whether thermodynamic scaling is valid for others short-time dynamical properties that have been considered in different theories that relate short- and long-time dynamics of glass-forming liquids.
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