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Structural relaxation and dynamical correlations in a molten state near the liquid-glass transition: A molecular dynamics study

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Molecular dynamics calculations have been used to study structural relaxation and dynamical correlations near the glass transition in the system $[\text{Ca}(\text{NO}_3)_2]_{0.4}[\text{KNO}_3]_{0.6}$. As in a typical molten salt, the overall structure is determined by charge ordering. However, the radial distribution function for Ca^{2+} ions is unusual in that even at high temperatures it shows a split first peak due to specific spatial correlations of the cations with the nitrate anions. Structural relaxation that accompanies cooling of the system has been characterized with the aid of the van Hove real-space correlation functions $G_s(r,t)$ for the constituent atoms (Ca, K, N, O). The relaxation of the incoherent structure factor $F_s(k,t)$, with a wave vector k near the peak of the static structure factor, has been investigated as a function of temperature. The results clearly reveal both the α and β relaxation processes; the former can be well represented by a master curve with a stretched exponential shape. An analysis of the susceptibility, which agrees qualitatively with neutron spin-echo data, suggests that the glass transition for the model occurs around 400 K. The relatively small discrepancy with the experimental transition temperature derived from neutron scattering data (366 K) is likely related to inadequacies in the model employed for the interionic interactions. The functions $C_1(t)$ and $C_2(t)$, which describe the reorientational relaxation of the threefold symmetry axes of the nitrate ions, are shown to exhibit a scaling behavior analogous to that of the structure factor. In the region of the glass transition, where translational diffusion has essentially stopped, the nitrate ions continue to flip predominantly about their twofold axes.

I. INTRODUCTION

The dynamical properties of supercooled liquids and the glass transition have received considerable attention, both from theoretical and experimental points of view. In addition, detailed computer simulations studies on idealized models have also contributed to our understanding of the field.¹ Recent theories of supercooled liquids, such as those based on mode-coupling schemes, describe the glass transition as an ideal ergodic to nonergodic transition occurring at a well-defined temperature; this transition is triggered by the nonlinear feedback mechanism governing the relaxation of density fluctuations, and is smeared by the existence of activated processes which restore ergodicity on a long time scale. Besides the existence of such a transition, mode-coupling theories predict the appearance, close to the transition, of two slow-relaxation steps (i.e., slow on the time scale of phonon motion).² The first of these two steps should exist on both sides of the transition temperature T_c and slow down critically with a characteristic time τ' . The second step exists only on the liquid side and when T_c is approached, the divergence of the associated time scale $\tau \gg \tau'$. There is also a divergence of the transport coefficients.² The similarity of susceptibility spectra to experimental dielectric loss data has led to the traditional, but somewhat misleading, terminology of the glass literature: namely, the second step is called α or primary relaxation and the first step is called β or secondary

relaxation. In this paper, we shall use the term " β -relaxation" to mean "first slow-relaxation step". Although this relaxation is very likely linked to the experimentally observed β -peaks such a link has not yet been demonstrated for any microscopic model.

A number of the theoretical predictions have been at least qualitatively confirmed by neutron scattering experiments⁴⁻⁶ and computer simulations on simple models.⁷⁻¹⁰ The large time window explored by time-of-flight and spin-echo neutron scattering experiments^{4,6} allows a detailed analysis of the scaling behavior near the glass transition. Although a comparable range of times cannot usually be explored with molecular dynamics simulations such calculations can nevertheless yield valuable complementary information on the nature of microscopic dynamical processes in glassy systems.

In this paper, we present the results of molecular dynamics calculations on the behavior of supercooled $[\text{Ca}(\text{NO}_3)_2]_{0.4}[\text{KNO}_3]_{0.6}$. The excellent glass-forming ability of this fused salt has made it the object of numerous experimental studies, in addition to the neutron scattering experiments already mentioned.¹¹⁻¹⁴ The relative simplicity of the constituent species in this so-called "fragile" liquid¹⁴ makes it an ideal candidate for a detailed study by molecular dynamics. Section II presents the interaction potentials and outlines the simulation procedures employed in the present work. The validity of the model is discussed in the light of density and sound velocity data, and results for the static pair structure are presented. Section III deals with single particle diffusion, Sec. IV with the relaxation of the pair structure, and Sec. V with the rotational motion of the nitrate ions. The article ends with a brief discussion.

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TABLE I. Potential parameters.^a

| Atom, <i>i</i> | A_{ii} (MJ mol ⁻¹) | B_{ii} (Å ⁻¹) | C_{ii} (kJ mol ⁻¹) | q_i (e) |
|----------------|-------------------------------------|--------------------------------|-------------------------------------|----------------|
| Ca | 151.0 | 3.05 | 1464 | 2.00 |
| N | 140.8 | 3.78 | 1084 | 0.95 |
| O | 260.0 | 4.18 | 1085 | -0.65 |
| K | 151.0 | 2.967 | 1464 | 1.00 |

^aCross-interaction parameters A_{ij} , C_{ij} were obtained from the geometric mean of the ii and jj parameters; B_{ij} parameters from the arithmetic mean [The parameters were provided by M. Ferrario (private communication, 1988)].

II. MOLECULAR DYNAMICS CALCULATIONS

A. Technical details

The simulation system consisted of 192 K⁺, 128 Ca²⁺ and 448 NO₃⁻ ions contained in a cubic box and interacting via atom-atom and charge-charge potentials of the type

$$V(r) = A_{ij} \exp(-B_{ij}r) - C_{ij}/r^6 + q_i q_j / r. \quad (1)$$

The atom-atom potential parameters are listed in Table I. The anion parameters are similar to those used in a recent study of NaNO₃.¹⁵ The cations carried their full charges and NO₃⁻ was treated as a rigid unit with fractional charges (q_i) on the N and O atoms.¹⁵ No polarizability effects were considered. Periodic boundary conditions were imposed, and the long-range electrostatic interactions between the ions were computed using the Ewald method. Most of the simulations were carried out under constant-pressure constant-temperature conditions following the extended system method introduced by Nosé.¹⁶ The time step used for the integration of the dynamical equations was 10⁻¹⁴ s.

The sample of 768 ions was first equilibrated for 10 ps at $T = 2000$ K and $V = 34\,138$ Å³. Then a 30 ps run was carried out to determine the equilibrium properties corresponding to this state condition. Next, with the volume held constant, the temperature was rescaled to 800 K, and a 10 ps equilibration trajectory was run. A subsequent 40 ps trajectory was then stored for analysis. These two runs effectively constituted the preparation of the system. The study of the glass transition began with a sequence of cooling-equilibration-run cycles, carried out under constant-pressure conditions, which eventually brought the system temperature to 700, 600, 550, 450, and 350 K, respectively. The presence of long-range Coulomb interactions meant that the calculation times were rather long and hence the effective cooling rate was necessarily rather rapid, being of the order of 10¹² K/s.

TABLE II. Molecular dynamics results.

| Ensemble | $\langle T \rangle$ (K) | $\langle p \rangle$ (kbar) | $\langle U \rangle$ (10 ⁻¹⁶ J) | $\langle V \rangle$ (Å ³) | Equilibration (ps) | Run length (ps) |
|------------|----------------------------|-------------------------------|--|--|-----------------------|--------------------|
| <i>NVT</i> | 2000 | 0.00 | -2.236 | 34138 | 10 | 30 |
| <i>NVT</i> | 800 | -0.31 | -2.498 | 34138 | 10 | 40 |
| <i>NpT</i> | 700 | -0.32 | -2.529 | 33185 | 20 | 50 |
| <i>NpT</i> | 600 | -0.29 | -2.559 | 32026 | 20 | 50 |
| <i>NpT</i> | 550 | -0.28 | -2.572 | 31619 | 170 | 100 |
| <i>NpT</i> | 450 | -0.27 | -2.643 | 30982 | 65 | 250 |
| <i>NpT</i> | 350 | -0.25 | -2.657 | 30556 | 120 | 300 |

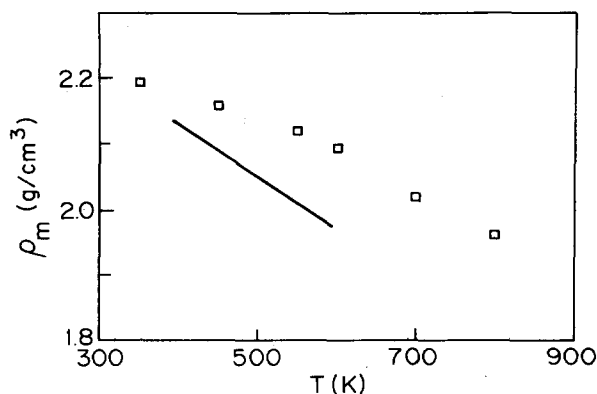


FIG. 1. Temperature dependence of the mass density of [Ca(NO₃)₂]_{0.4}[KNO₃]_{0.6}. The solid line is a fit to the experimental data (Ref. 12) and the squares are the molecular dynamics results.

The primary molecular dynamics data are summarized in Table II.

B. Validity of the model

As a prelude to the study of the glass transition we tested the ability of the model to represent real [Ca(NO₃)₂]_{0.4}[KNO₃]_{0.6}. The calculated zero-pressure mass density ρ_m is presented in Fig. 1. In the range of the limited experimental data,¹³ the simulation results are about 5% too high. This observation suggests that the interionic interactions are too strong and that as a consequence the system is too tightly "coupled." A curve drawn through the calculated $\rho_m(T)$ points changes slope around 500 K. This feature is sometimes used as a diagnostic for the glass transition but it actually signifies the temperature at which the relaxation time for volume changes has become comparable to the simulation time.¹ Anticipating our results we will see that there is evidence for continued slow structural relaxation below this temperature and that the transition temperature for the model is actually around 400 K.

In view of the recent neutron experiments,^{4,6} we shall be mostly interested in the long-time behavior of time-dependent properties. However, before proceeding to a discussion of the long-time behavior we first compare the short-time dynamical properties of the model with experimental data. The velocity of longitudinal sound was estimated from the short-time oscillations in $F(k,t)$, the density-density dynamical structure factor with $k \approx 0.2$ Å⁻¹, the smallest wave vector compatible with the periodic boundary conditions. The calculated sound velocities ranged from 3300 ms⁻¹ at 450 K to 2500 ms⁻¹ at 600 K whereas the corresponding

experimental values from Brillouin data range from 2500 to 1800 ms^{-1} .¹¹ This discrepancy in the molten salt is a further indication of the exaggerated stiffness of the model (recall the mass density plotted in Fig. 1), but is likely also partly due to the use of high frequency (10^{12} s^{-1}) oscillations to estimate the sound velocity. At the lowest temperature studied, where the discrepancy in the density is smallest (see Fig. 1), the calculated sound velocity (3500 ms^{-1}) is in better agreement with the measured value.

As a further check on the model, Fig. 2 presents a comparison between the neutron time-of-flight spectrum⁴ and that obtained from power spectra of the atomic velocity autocorrelation functions weighted by their appropriate neutron scattering cross sections. Apart from a high frequency shoulder, which is absent from the simulation result, the broad features of the phonon contribution are correctly reproduced. The discrepancy at high frequency is possibly due to multiphonon processes and the absence of internal modes in the rigid model employed for the NO_3^- ion.

From the above mentioned results, we conclude that the interaction potentials of Table I provide at least a semiquantitative description of $[\text{Ca}(\text{NO}_3)_2]_{0.4}[\text{KNO}_3]_{0.6}$. However, since the interionic coupling appears to be slightly too strong, we would expect that the behavior of the model at a given temperature will likely correspond to that of the real system at a slightly lower temperature.

C. Static structure

The structure of a fused salt at different temperatures is best studied by means of $g_{\alpha\beta}(r)$, the distribution functions for different pairs of atoms α - β . The simulations indicate that the basic liquid-like structure is retained when the fused salt is cooled below 800 K. In particular, the peak positions in $g_{\alpha\beta}(r)$ shift only slightly as the temperature and volume decrease and the main peaks are fairly broad at all temperatures. No evidence of crystallization of the sample was detected during any of the runs. There is, however, one striking

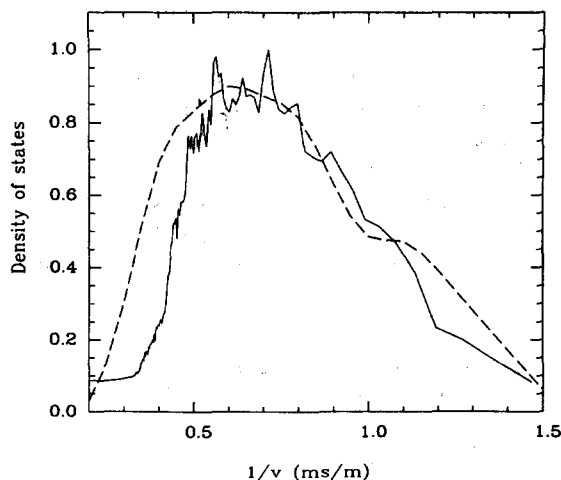


FIG. 2. Phonon density of states (in arbitrary units) for glassy $[\text{Ca}(\text{NO}_3)_2]_{0.4}[\text{KNO}_3]_{0.6}$ plotted as a function of the inverse velocity of the scattered neutrons in a time-of-flight experiment. The full curve is the neutron-weighted power spectrum constructed from the atomic velocity auto correlation functions. The dashed curve is the experimental result from Ref. 4.

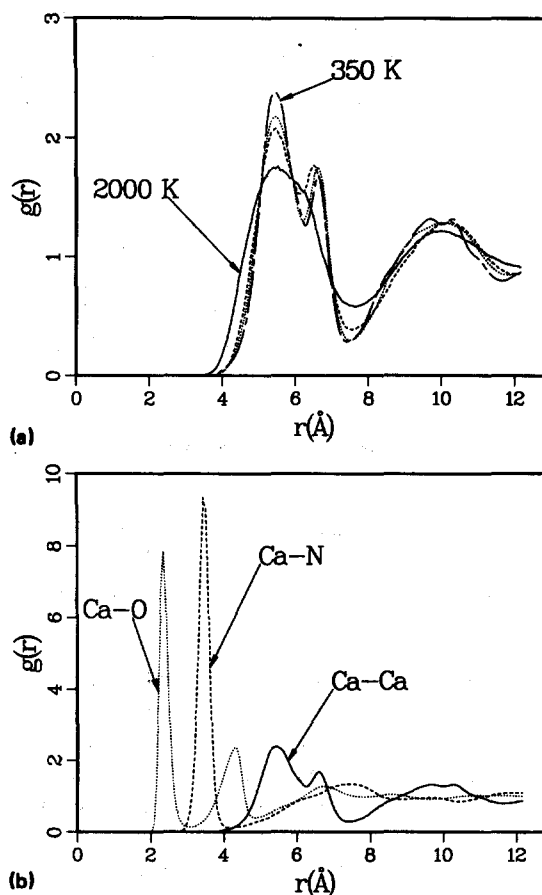


FIG. 3. (a) Radial distribution functions for Ca-Ca at various temperatures: 2000 K (full), 800 K (dashed), 550 K (dots) and 350 K (long dashes), respectively. The split first peak should be noted. (b) Atom-atom radial distribution functions for Ca-O, Ca-N, and Ca-Ca at 350 K.

structural feature present, namely, a split first peak in the curve for Ca-Ca pairs which is illustrated in Fig. 3(a). Distribution functions for Ca-O and Ca-N at 350 K are shown in Fig. 3(b). The alternating pattern of negative and positive shells, characteristic of molten salts, is clearly visible. The position and area under the first Ca-O and Ca-N peaks indicate that NO_3^- is surrounded on average by 2.2 Ca^{2+} ions, with the Ca-N vector forming a small angle ($\sim 20^\circ$) with the molecular plane. The $g(r)$'s for K-N and K-O pairs at the same temperature (not shown) yield a coordination number of 7.5 for K^+ around each NO_3^- , but with a much less well-defined structure. The split peak in the $g(r)$ for Ca-Ca shown in Fig. 3 cannot be directly related to the onset of the glassy phase because it is already present even at 800 K. A more detailed analysis of the simulation data indicates that the double peak arises from the existence of two preferred arrangements of the closest pair of Ca^{2+} neighbors to a given NO_3^- ion. Essentially, the two Ca^{2+} ions can be either on the same side or on opposite sides of the NO_3^- molecular plane.

III. TAGGED PARTICLE DYNAMICS

A. Diffusion

In order to estimate D_α , the diffusion coefficients of the different species α , we have calculated the atomic mean-square displacements

$$\Delta r_\alpha^2(t) = \langle |r_\alpha(t) - r_\alpha(0)|^2 \rangle. \quad (2)$$

The asymptotic temporal behavior of $\Delta r_\alpha^2(t)$ is given by $6D_\alpha t$. Calculated values of $\Delta r_\alpha^2(t)$ for the species Ca^{2+} are presented in Fig. 4. The diffusion coefficient is seen to decrease very rapidly with T ; it ranges from $9.0 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at 700 K to $6.9 \times 10^{-8} \text{ s}^{-1}$ at 550 K. Below $T = 550 \text{ K}$, the value of D is sufficiently small that it is affected by large statistical uncertainties. Values of D for the other species at 700 K are 3.1×10^{-6} for K^+ and $2.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for NO_3^- .

B. van Hove function

A more detailed picture of the diffusion can be obtained from the van Hove self-correlation functions $G_{\text{sa}}(r, t)$, defined as

$$G_{\text{sa}}(r, t) = \langle \delta[r_\alpha(t) - r_\alpha(0)] \rangle. \quad (3)$$

In a liquid, $G_{\text{sa}}(r, t)$ relaxes to 0 at long times, asymptotically approaching a Gaussian shape, with a width $D_\alpha t$. In a solid, $G_{\text{sa}}(r, t)$ levels off to a finite value at long times, the width being related to the Lindemann ratio. Figure 5 presents results for Ca^{2+} at different temperatures. The maximum of $r^2 G_{\text{sa}}(r, t)$ indicates the most probable position of the particle α at time t which was at the origin at $t = 0$. In Fig. 5(a), this maximum is clearly drifting with increasing times, indicating liquid-like behavior at 600 K. A slight drift is still evident in Fig. 5(b). This temperature (450 K) is below the point where a curve drawn through the $\rho_m(T)$ of Fig. 1 would have a change in slope. The $T = 350 \text{ K}$ results shown in Fig. 5(c) are characteristic of a structure that is virtually arrested on the time scale of the simulation. The other species display a very similar behavior, except for oxygen, whose $G_{\text{sa}}(r, t)$ has a peculiar double-peaked structure due to the rotation of the nitrate ions (see Fig. 6). This rotation, which is present at all temperatures, will be explored more fully in Sec. V. The results for $\Delta r_\alpha^2(t)$ and $G_{\text{sa}}(r, t)$ give an indication of a transition from ergodic (liquid like) to a non-

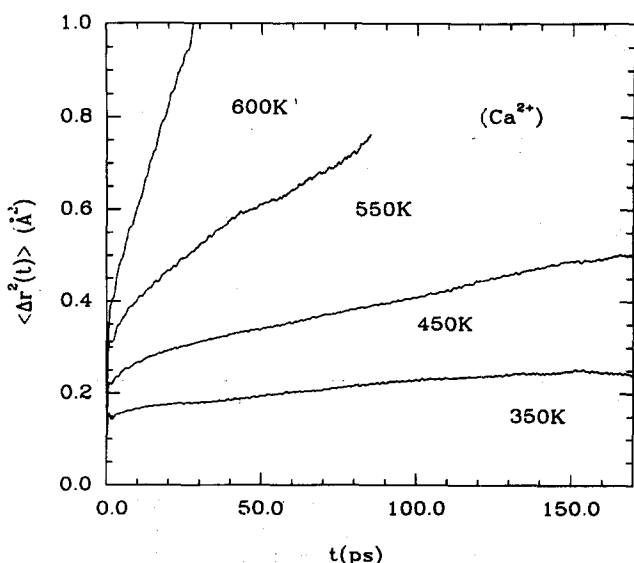
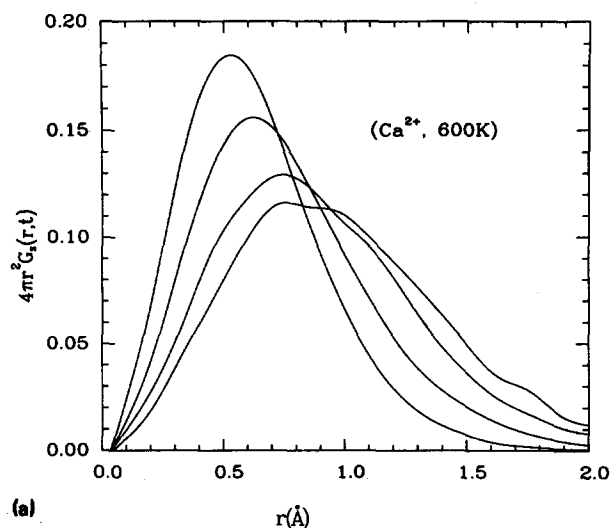
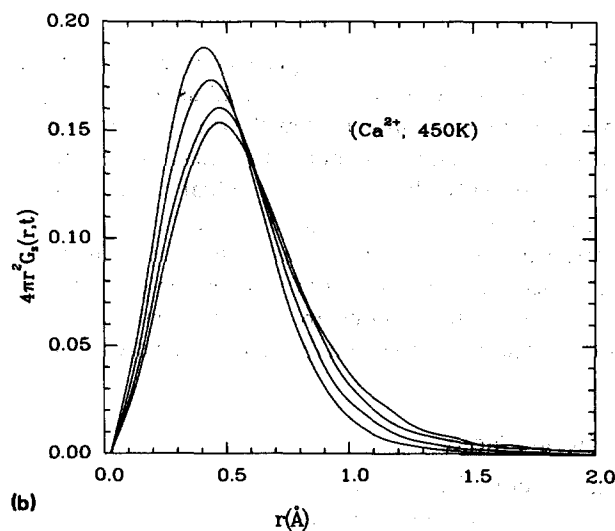


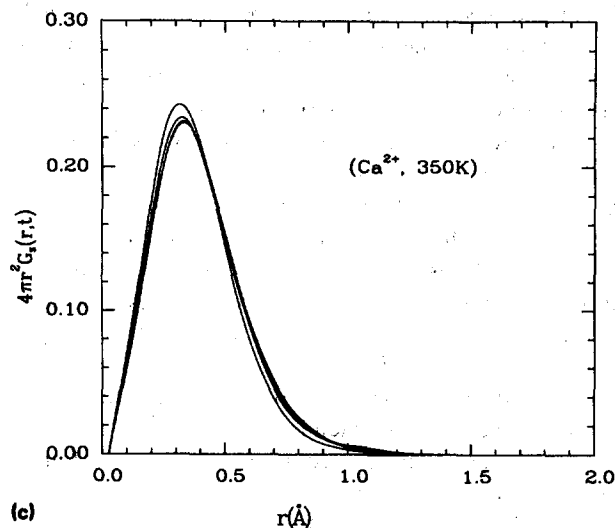
FIG. 4. Mean-square displacements of Ca^{2+} ions as a function of time at various temperatures.



(a)



(b)



(c)

FIG. 5. The van Hove real-space self-correlation function for Ca^{2+} ions at (a) 600 K; $t = 5, 15, 30,$ and 45 ps, respectively. (b) 450 K; $t = 20, 120, 180,$ and 240 ps, respectively. (c) 350 K; $t = 20, 60, 120,$ and 280 ps, respectively.

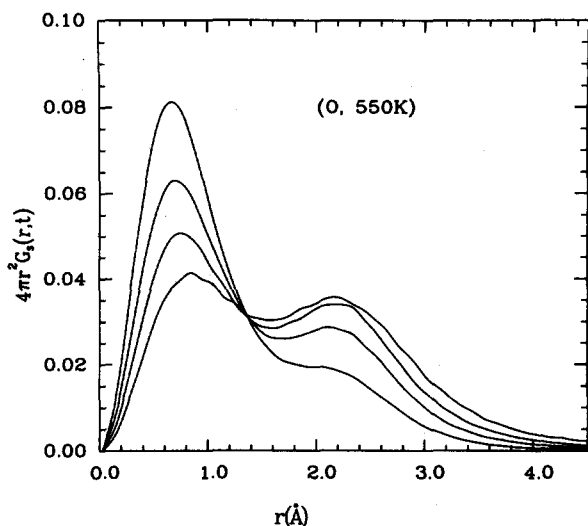


FIG. 6. The van Hove real-space self-correlation function for oxygen atoms at 550 K for $t = 10, 30, 60,$ and 90 ps, respectively.

ergodic (glassy) behavior taking place between $T = 450$ K and $T = 350$ K. Activated hopping-like diffusion, which was observed to become dominant below the transition in a comparable study of a soft sphere fluid,⁹ is virtually absent from our results. Actually, the study of individual trajectories revealed the presence of very rare jumps for K^+ ions, even at $T = 350$ K; an observation consistent with the experimentally determined residual conductivity below the glass transition.¹² However, these jumps are so infrequent that their quantitative study is far beyond the reach of the present simulation.

C. Scattering factor

The structure factor for incoherent neutron scattering is defined as the spatial Fourier transform of $G_{sa}(r,t)$

$$F_{sa}(\mathbf{k},t) = \langle \exp \{i\mathbf{k} \cdot [\mathbf{r}_\alpha(t) - \mathbf{r}_\alpha(0)]\} \rangle. \quad (4)$$

In simulations, this quantity can be obtained with much better accuracy than the coherent scattering factor which is experimentally accessible. However, for atomic systems, and for wavevectors near the peak in the structure factor \mathbf{k}_0 , both the coherent and incoherent responses usually display a similar time dependence. Accordingly, if one examines the response for Ca^{2+} ions only, rather than that of some weighted average over all species present, one can reasonably compare $F_{sa}(\mathbf{k}_0,t)$ results for Ca^{2+} ions to the neutron scattering data reported in Ref. 4. This restriction is necessary since averaging the incoherent structure factor over all species α would likely result in a decay of $F_{sa}(\mathbf{k}_0,t)$, due to the oxygen atom contribution arising from rotational motion of the nitrate ions; a process which is observed in both the liquid and in the glass. Since this rotational motion was found to consist mainly of rapid flipping of molecules around their twofold axes (i.e., the NO bonds—see Sec. V), it will likely have only a modest influence on the collective properties measured by neutron scattering. Figure 7 shows $F_{sa}(\mathbf{k}_0,t)$ for Ca^{2+} ions at $\mathbf{k}_0 = 1.74 \text{ \AA}^{-1}$ which should be compared to the neutron results displayed in Fig. 3 in Ref. 4. Three relaxation steps can be clearly distinguished. The first,

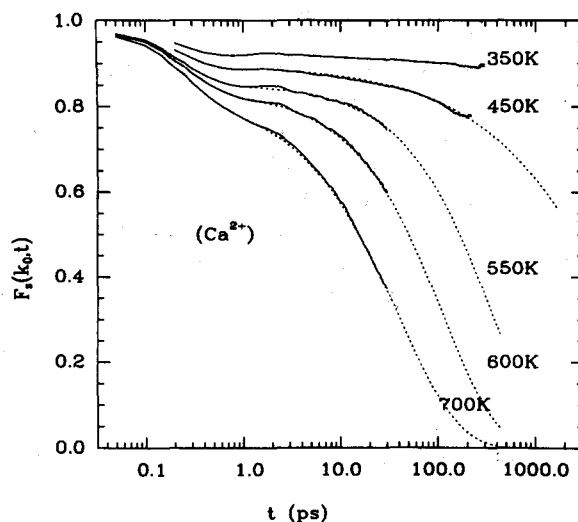


FIG. 7. The temperature dependence of $F_s(k_0,t)$ for Ca^{2+} ions for $k_0 = 1.74 \text{ \AA}^{-1}$. The dashed lines indicate the fitted curves used to extrapolate the data and to calculate the spectra shown in Fig. 9 (see the text).

which is almost independent of temperature, occurs on time scales $t < 0.5$ ps, typical of inverse phonon frequencies. The second step, which is characterized by a positive curvature of $F_{sa}(\mathbf{k}_0,t)$ in a semilog plot, becomes more pronounced as T decreases. This feature can be identified with the β relaxation process. The third relaxation step, or α relaxation, slows down considerably when T decreases. It appears in the simulations at high temperatures but only its very beginning can be discerned at $T = 450$ K.

The scaling features of the α relaxation process, both predicted by mode-coupling theories² and observed experimentally,⁶ are illustrated in Fig. 8. By translating the curves obtained at different temperatures on a logarithmic scale, a master curve $f(x)$ can be obtained with the form

$$F_s(k_0,t;T) = f(x) = f[t/\tau(T)]. \quad (5)$$

In the present case, f is well approximated by a Kohlrausch law,

$$f(x) = 0.90 \exp(-x^{0.61}). \quad (6)$$

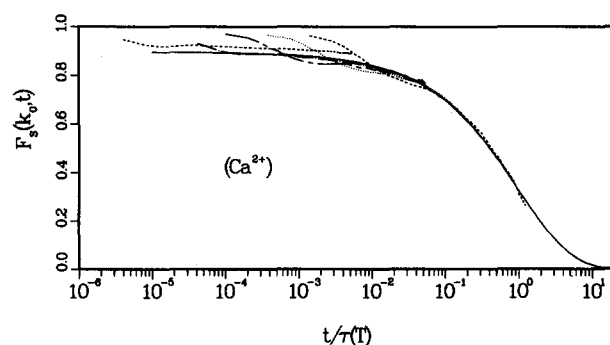


FIG. 8. The master curve fit to $F_s(k_0,t)$ for Ca^{2+} ions with $k_0 = 1.74 \text{ \AA}^{-1}$. The bold curve indicates the Kohlrausch law, $f(x) = 0.90 \exp[-x^{0.61}]$ where $x = t/\tau(T)$. The dashed and dotted curves are from Fig. 7 and from left to right refer to 350, 450, 550, 600, and 700 K, respectively. The curve for $T = 350$ K lies systematically above the master curve suggesting that at this temperature the system is in a glassy state.

In reality, the scaling hypothesis has been assumed in order to obtain the master curve (Eq. 6). However, the consistency of the results and the reasonable relaxation times that follow suggest that, at least for wave vectors around k_0 , the value of $\beta \approx 0.6$ is appropriate for all temperatures considered. The relaxation curves could almost certainly be fitted by other functional forms but, in practice, scaling has to be assumed since we have such a limited data set.

The curve for $T = 350$ K in Fig. 8 appears to lie well above the master curve obtained for higher temperatures, which is a further indication of the glassy character of the system at this state point.⁹ The temperature-dependent relaxation times $\tau(T)$ that appear in Eq. (5) are of the same order of magnitude as typical diffusion times ($\tau^{-1} = Da^{-2}$, where a is a jump distance), but unfortunately, in the present case, the uncertainties on the calculated diffusion constants (recall Fig. 4) do not allow their *a priori* use as a scaling parameter, as was done in the analysis of the neutron data.⁶ Instead, values for $\tau(T)$ have been obtained from a best fit procedure using Eq. (5). Except for $T = 450$ K, the values of $\tau(T)$ obey (roughly) the relation $\tau(T) = (Da^{-2})^{-1}$ with $a = 2 \text{ \AA}$. These diffusion times are much larger than the shear relaxation time τ_s , estimated from experimental sound velocity and viscosity data.¹¹ However, a comparable order of magnitude for τ_s results if we take values for the viscosity derived from the Stokes-Einstein relation and the calculated diffusion coefficient, plus the experimental value for the high frequency shear modulus. Relaxation times derived from the master curve analysis of $F_s(k_0, t)$ for *nitrogen* atoms are shown in Fig. 14 (Sec. V), where they are compared with rotational relaxation times of nitrate ions.

In view of the exponential decay observed for $T > 500$ K in recent light scattering experiments (L. Torell, private communication) the non-exponential decay shown in Fig. 7, at 700 K, is somewhat surprising. This apparent contradiction can be understood from the fact that for small wave vectors, the hydrodynamic limit (and thus the exponential decay) are recovered much closer to T_c . Indeed, a master curve analysis performed on a soft sphere system for different k values yielded a Kohlrausch exponent $\beta \approx 1$ for the smallest k considered.⁸ The master curve shown in Fig. 8 differs in detail from the corresponding experimental one.⁶ However, this is not entirely unexpected since the simulation and experiment are actually measuring different properties and the α relaxation is known to depend on the quantity considered.

The existence of two different slow relaxation steps manifests itself in the frequency spectrum of $F_s(k_0, t)$ by the existence of a minimum in the susceptibility

$$\chi''(k_0, \omega) = \omega \int dt \exp(i\omega t) F_s(k_0, t) = \omega S_s(k_0, \omega). \quad (7)$$

In Fig. 9, $\log \chi''(k_0, \omega)$ is plotted vs $\log \omega$. To obtain the required Fourier transform, the calculated results for $F_s(k_0, t)$ have been artificially smoothed and extrapolated to longer times using Kohlrausch functions fitted to data for each temperature. The fitted curves are indicated by the dashed lines in Fig. 7. The susceptibility (χ'') curves shown in Fig. 9 are very similar to the experimental ones reported in

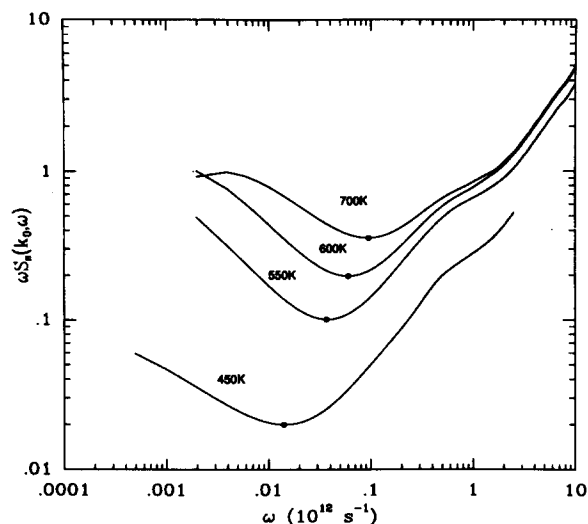


FIG. 9. Temperature dependence of the susceptibility $\chi''(\omega) = \omega S_s(k_0, \omega)$ for Ca^{2+} ions from the fitted curves in Fig. 7. The dots indicate minima in the respective curves.

Fig. 4 of Ref. 4. The position of ω_{\min} , the minimum in χ'' , varies rapidly with temperature, indicating the slowing down of the two relaxation processes. The relatively restricted frequency range of the simulation data does not allow a detailed scaling analysis of the results similar to the one performed in Ref. 4. However, it is interesting to note that the minima of the curves in Fig. 9 appear to lie on a straight line; a feature predicted by mode-coupling theories.² According to these theories, both ω_{\min} and χ_{\min} are expected to vary as power laws of $\epsilon = T - T_c$, where T_c is the critical temperature for the ergodic-nonergodic transition. In the present case, an extrapolation of the positions of the minima suggests $T_c = 400$ K; a value which is in reasonable agreement with the experimental result $T_c = 366$ K from derived from neutron scattering data.^{4,6}

Another interesting feature of the χ'' spectrum shown in Fig. 9 is the presence of a shoulder around $0.5 \times 10^{-12} \text{ s}^{-1}$. This feature is very reminiscent of the so-called beta peak which is often observed in dielectric relaxation experiments at lower frequencies and closer to the transition.¹⁷ Anticipating our results we will see that a similar feature is also present in the susceptibility spectrum of the orientational relaxation function $C_2(t)$ (see Sec. V, Fig. 15).

IV. COLLECTIVE DYNAMICS

The collective dynamics of the system has been investigated with the aid of the van Hove distinct correlation functions $G_d(r, t)$ defined as

$$\rho G_{d\alpha\beta}(r, t) = \left\langle \sum_y \delta[\mathbf{r}_{i\alpha}(t) - \mathbf{r}_{j\beta}(0) - \mathbf{r}] \right\rangle / N_{i\alpha} N_{j\beta}. \quad (8)$$

For $t = 0$, $G_{d\alpha\beta}(r, t)$ reduces to $g_{\alpha\beta}(r)$, the pair distribution function for the pair of atoms α - β . In a liquid, $G_d(r, t)$ decays to 1 at long times but in a glass a "frozen-in" structure persists for very long times. The Ca-N correlation functions are displayed in Fig. 10 for $T = 450$ K. Even at high temperatures, structural relaxation is quite slow with a well-

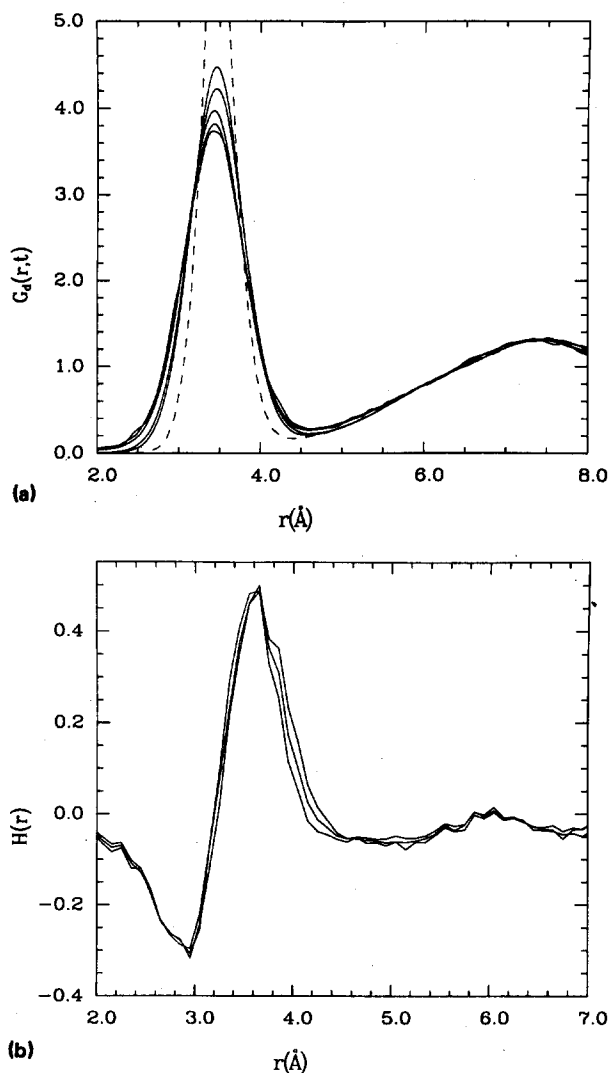


FIG. 10. (a) The time dependence of the van Hove function $G_d(r,t)$ for Ca-N atom pairs at $T = 450$ K. The full curves are for $t = 2, 20, 120, 180,$ and 240 ps, respectively and the dashed curve is $g(r)$. (b) The function $\{G_d(r,t) - G_d(r,180 \text{ ps})\}$ at $T = 450$ K for $t = 20, 30,$ and 40 ps, respectively. The latter two curves have been rescaled by an r -independent factor.

defined structure remaining after 50 ps. At 450 K, a relatively fast decay ($t < 50$ ps) corresponding to the first and second relaxation steps in $F_s(k_0, t)$, is followed by a plateau. The beginning of the α relaxation process which was observable in $F_s(k_0, t)$ is not present here indicating that the time scale for the α relaxation of collective properties is longer than for single particle properties.⁷

The plateau value for $G_d(r,t)$, which is very similar at $T = 350$ K and $T = 450$ K, differs from the initial value $g(r)$ only for the first neighbor shell ($r < 5 \text{ \AA}$). A similar behavior is observed for other atom pairs. Since the difference between $g(r)$ and the plateau value is due to the combination of the short-time relaxation and the β relaxation, the present results are consistent with the usual description of the β relaxation as a localized process, involving the motion of a restricted number of atoms.¹⁷

The decay of $G_d(r,t)$ to its plateau value at $T = 450$ K has been studied by monitoring the behavior of the difference $[G_d(r,t) - G_d(r,t = 180 \text{ ps})]$ for different times t . According to mode-coupling theory, in the β relaxation regime,

this quantity should have the factorized form

$$G_d(r,t) - G_d(r,180 \text{ ps}) = H(r)[f(t) - f(180)]. \quad (9)$$

Such behavior is, in fact, observed in the present calculations. Figure 10(b) shows that the curves obtained for different times appear to coincide once they are rescaled by an r -independent factor. The resulting universal curve is strikingly similar to the $H(r)$ function recently calculated for hard spheres.¹⁸

V. ORIENTATIONAL RELAXATION

The analysis of the $G_s(r,t)$ plot for oxygen atoms (recall Fig. 6) indicated the existence of important reorientational motions of NO_3^- ions at all temperatures. We have analyzed this motion in more detail by computing the distribution function for the tilting angle of the molecular plane $\theta(t)$ defined as

$$\theta(t) = \cos^{-1}[\mathbf{u}(t) \cdot \mathbf{u}(0)], \quad (10)$$

where $\mathbf{u}(t)$ is a unit vector perpendicular to the molecular plane at time t . The choice of $\theta(t)$ as the relevant orientational coordinate implies treatment of the nitrate ion as a symmetric top. The appropriate distribution function $G(\theta,t)$ is defined as

$$(1/2)\sin \theta * G(\theta,t)d\theta = \frac{dN(\theta,t)}{N}, \quad (11)$$

where $dN(\theta,t)/N$ is the fraction of molecules with a tilting angle between θ and $\theta + d\theta$ and $G(\theta,t)$ is normalized to 1 for a uniform distribution. For a symmetric top molecule, the function $G(\theta,t)$ can be expanded as

$$G(\theta,t) = \sum_L C_L(t) P_L(\cos \theta), \quad (12)$$

where $P_L(x)$ is the L th order Legendre polynomial and

$$C_L(t) = \langle P_L[\cos \theta(t)] \rangle. \quad (13)$$

In the case of diffusive reorientational motion

$$C_L(t) \approx \exp[-t/\tau_L] \quad (14)$$

with

$$\tau_L = \tau_0/[L(L+1)] \quad (15)$$

and $(1/2)\sin \theta G(\theta,t)$ —in analogy with the quantity $r^2 G_s(r,t)$ —has a maximum which moves towards larger angles as t increases.

In the simulations, a slow diffusive motion of θ is evident at high temperature [Fig 11(a), 700 K], together with larger angular jumps which populate the region between $\pi/2$ and π . As the temperature is decreased, angular diffusion slows down, and at 350 K [Fig. 11(b)] reorientation occurs almost exclusively through jumps of amplitude close to π . The different nature of the angular motion at the two temperatures is illustrated in sample molecular trajectories shown in Fig. 12. These clearly reveal the freezing of diffusion and the predominance of large amplitude jumps at 350 K. An analysis of the motion of NO bond vectors at this temperature indicated that these jumps involve mainly rotation about twofold axes. Jump motion about the threefold axis was also observed in the glass. However, this motion, which is independent of θ , was less prevalent and hence has

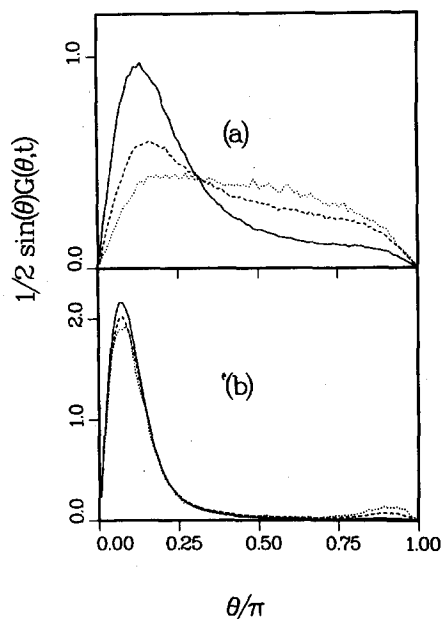


FIG. 11. The function $1/2 \sin \theta G(\theta, t)$. (a) $T = 700$ K; $t = 5$ ps (full curve), 20 ps (dashed curve) and 40 ps (dotted curve). (b) $T = 350$ K; $t = 20$ ps (full curve), 100 ps (dashed curve) and 280 ps (dotted curve).

not been considered further in the following discussion.

A measure of the time scale of molecular reorientations can be obtained from the study of the relaxation of the coefficients $C_1(t)$ and $C_2(t)$ defined in Eq. (13). The behavior of the latter, shown in Fig. 13, reveals the same three-step structure as found previously for $F_s(\mathbf{k}_0, t)$ (Sec. III C). The α relaxation (long time) branches of the functions $C_1(t)$ and $C_2(t)$ can be fitted to Kohlrausch form

$$\begin{aligned} C_1(t) &= 0.89 \exp[-(t/\tau_1)^{0.61}], \\ C_2(t) &= 0.76 \exp[-(t/\tau_2)^{0.42}]. \end{aligned} \quad (16)$$

The corresponding rotational relaxation times τ_1 and τ_2 are plotted in Fig. 14 as functions of temperature, together with the translational diffusion times of the NO_3^- center of

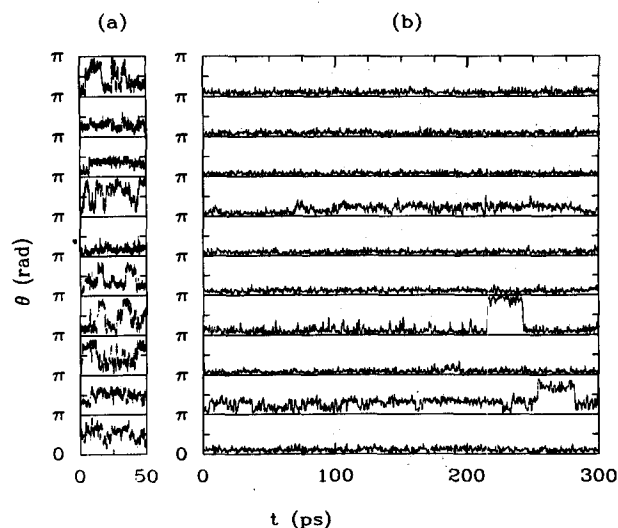


FIG. 12. $\theta(t)$ trajectories for selected nitrate ions at (a) $T = 700$ K and (b) $T = 350$ K. These curves do not necessarily provide a statistically representative sample.

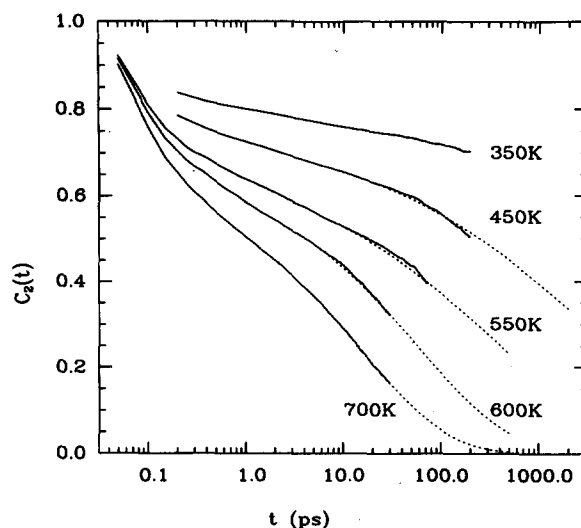


FIG. 13. Temperature dependence of the orientational relaxation function $C_2(t)$. The dashed lines indicate the fitted curves used to calculate the spectra shown in Fig. 15 (see the text).

mass obtained from the master curve analysis of $F_{sa}(\mathbf{k}_0, t)$ for nitrogen atoms. At 600 K and above, the predominance of large angular jumps is reflected in the value of the ratio τ_1/τ_2 which is close to 1, as predicted for this type of relaxation,¹⁹ in contrast to the value of 3 associated with diffusive behavior; recall Eq. (15). As the temperature is lowered the most probable motion involves rotational jumps of about π radians. However, the relaxation of $C_2(t)$ —which is unaffected by flips of π —slows down more rapidly than that of $C_1(t)$ and hence the ratio τ_2/τ_1 tends to diverge.

The susceptibility spectrum of $C_2(t)$ has been calculated with the same smoothing and extrapolation procedure which was used previously for $F_s(\mathbf{k}_0, t)$. The resulting susceptibility $\chi_2''(\omega)$ is plotted in Fig. 15. As with the (translational) susceptibility shown in Fig. 9, $\chi_2''(\omega)$ displays a low-frequency minimum which varies rapidly with temperature, and a shoulder at higher frequency.

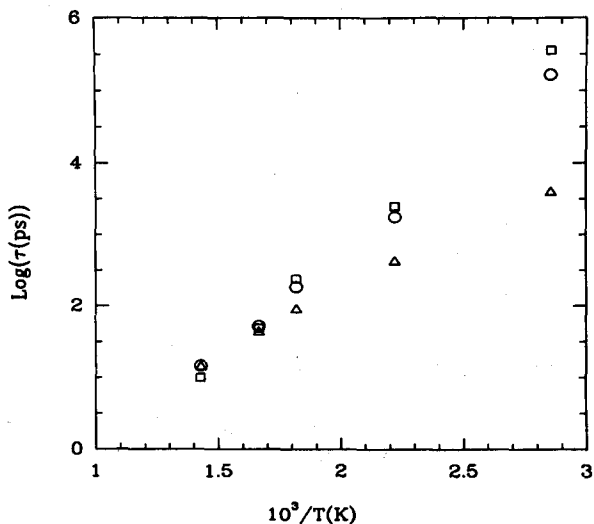


FIG. 14. Temperature dependence of characteristic times for nitrate ion translational (circles) and reorientational relaxation functions $C_1(t)$ (triangles) and $C_2(t)$ (squares). The lowest temperature data points are subject to considerable numerical uncertainty.

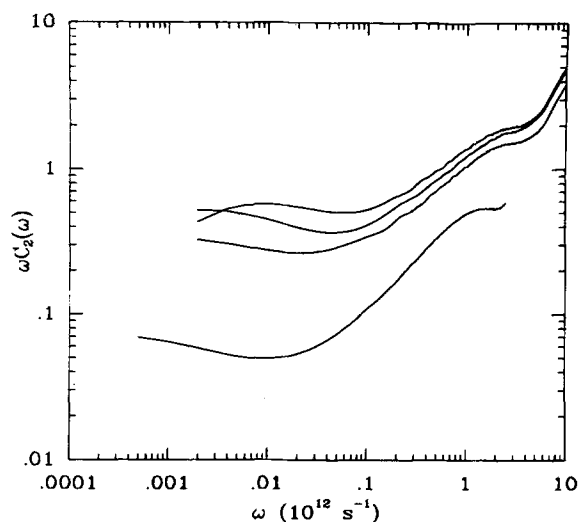


FIG. 15. Temperature dependence of the susceptibility $\chi_2''(\omega) = \omega C_2(\omega)$, derived from the functions $C_2(t)$ shown in Fig. 13 (see the text). Curves from top to bottom refer to 700, 600, 550, and 450 K, respectively.

The rotational motion of NO_3^- ions has been investigated experimentally using conventional Raman scattering.²⁰ Below the glass transition, the polarized and depolarized Raman lines of a totally symmetric intramolecular vibrational band can be superimposed, within the experimental resolution, indicating that orientational relaxation in the glass is occurring on a time scale longer than about 100 ps. This finding is in agreement with the present simulation results discussed above. Recently, temperature dependent Brillouin scattering data have been interpreted to indicate that rotational and translational motions decouple near the glass transition.¹¹ However, our calculations do not seem to support this suggestion. More precisely, the apparent decoupling we observe between the relaxation times for $C_1(t)$ and $C_2(t)$ can be explained by the existence of thermally activated flips of anion molecular planes. These flips persist at low temperature but in a first approximation should not affect the Brillouin intensities. An alternative interpretation, is that the broad central line observed in the Brillouin spectrum, and previously taken as an indication of relatively fast orientational relaxation,¹¹ is actually related to the relaxation occurring at frequencies typical of the minimum in the susceptibility spectrum, i.e., the β relaxation and possibly even the beginning of the α relaxation. The time scale for the α relaxation is thought to be much longer for the long-wavelength quantity measured in Brillouin scattering than for the shorter-wavelength quantity probed in neutron scattering experiments. Hence, the central line associated with α relaxation is likely too narrow to be resolved in the Brillouin experiments. Unfortunately, techniques such as photon correlation spectroscopy,²¹ which could probe the relevant time scales and reveal the nonexponential shape of the relaxation, have not, to our knowledge, been used on this system.

VI. CONCLUSION

Motivated mainly by the availability of extensive experimental information, we have carried out a computer simulation study on the effect of cooling and the approach to the

glass transition in the fused salt $[\text{Ca}(\text{NO}_3)_2]_{0.4}[\text{KNO}_3]_{0.6}$. Our goal has been to achieve a microscopic interpretation of the various relaxation processes that have been reported. To do so we have employed a reasonably realistic model for the interionic interactions which in turn has placed extensive demands on the computation time. Accordingly, the cooling rate employed in this study was relatively rapid and the time domain explored was far less extensive than in recent neutron scattering experiments.^{4,6} Our main conclusion is a broad confirmation of the interpretation of the neutron results^{4,6} namely, that on the time scale of the simulations there exists a microscopic transition around 400 K. Detailed analysis of the dynamic structure factor $F_s(k_0, t)$ obtained from the molecular dynamics trajectories for Ca^{2+} ions, has demonstrated the existence of three relaxation regimes, two of them slowing down near the transition. Above the transition, the calculated α relaxation obeys a master curve of stretched exponential form; a finding that seems to be at odds with recent light scattering data.²²

The function $G_s(r, t)$, which has recently been shown to be a valuable diagnostic of the glass transition,⁹ has been employed here also. The structural arrest associated with the glass transition is evident for Ca^{2+} ions but this is not the case for oxygen atoms. For the latter, the function $G_s(r, t)$ exhibits a bimodal distribution that continues to relax even at the lowest temperature studied. This relaxation has been identified as due to the continued flipping of the NO_3^- ions about their twofold axes. Such a motion had been invoked previously in order to interpret light scattering data from this system.^{11,20} The nature of the orientational motion has been analyzed with the aid of the distribution function $G(\theta, t)$, where $\theta(t) = \cos^{-1}\{\mathbf{u}(t) \cdot \mathbf{u}(0)\}$ and \mathbf{u} is a unit vector perpendicular to the molecular plane. We have established that activated jump motion of the molecular planes occurs and that this motion is independent of the freezing of translation and rotational diffusion. Below the glass transition, flips of the molecular plane, i.e., jumps through π radians, predominate. The relaxation of the orientational correlation function $C_2(t)$ exhibits the same three-step structure on a similar time scale as $F_{s,N}(k_0, t)$, the density self-correlation function of nitrogen atoms. The analysis of the relaxation of $C_2(t)$ suggests a possible new interpretation of the central peak seen in the Brillouin spectrum.

The collective dynamics of the system has been probed. In the glassy state, as in simpler model systems, $G_d(r, t)$ was found to differ from $g(r)$ only at small distances.¹⁸

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- ¹C. A. Angell, J. H. R. Clarke, and L. V. Woodcock, *Adv. Chem. Phys.* **48**, 397 (1981); G. H. Fredrickson, *Annu. Rev. Phys. Chem.* **39**, 149 (1988).
- ²E. Leutheusser, *Phys. Rev. A* **29**, 2765 (1984); U. Bengtzelius, W. Gotze, and A. Sjölander *J. Phys. C* **17**, 5915 (1984); W. Götze and L. Sjögren, in *Dynamics or Disordered Materials* (Springer, Berlin, 1989); *J. Phys. Condensed Matter* **1**, 4183 (1989).
- ³T. R. Kirkpatrick *Phys. Rev. A* **31**, 939 (1985); T. R. Kirkpatrick and P. G. Wolynes *ibid.* **B36**, 8552 (1987); T. R. Kirkpatrick and D. Thirumalai, *J. Phys. A* **22**, L149 (1989).
- ⁴F. Mezei, W. Knaak, and B. Farago, *Eur. Phys. Lett.* **7**, 529 (1988).
- ⁵D. Richter, B. Frick, and B. Farago, *Phys. Rev. Lett.* **61**, 2465 (1988).
- ⁶W. Knaak, F. Mezei, and B. Farago, *Phys. Rev. Lett.* **58**, 571 (1987); F. Mezei, W. Knaak, and B. Farago, *Phys. Scripta T* **19**, 363 (1987).
- ⁷J. J. Ullo and S. Yip, *Phys. Rev. Lett.* **59**, 1509 (1985).
- ⁸B. Bernu, J.-P. Hansen, Y. Hiwatari, and G. Pastore, *Phys. Rev. A* **36**, 4891 (1987); G. Pastore, B. Bernu, J.-P. Hansen, and Y. Hiwatari, *ibid.* **38**, 454 (1988).
- ⁹J.-N. Roux, J.-L. Barrat, and J.-P. Hansen *J. Phys. Condensed Matter* **1**, 7171 (1989).
- ¹⁰J. J. Ullo and S. Yip, *Phys. Rev. A* **39**, 5877 (1989).
- ¹¹M. Grimsditch and L. M. Torell, in *Dynamics or Disordered Materials* (Springer, Berlin, 1989); L. M. Torell (private communication, 1988); M. Grimsditch, R. Bhadra, and L. M. Torell, *Phys. Rev. Lett.* **62**, 2616 (1989).
- ¹²F. S. Howell, R. A. Bose, P. B. Macedo, and C. T. Moynihan, *J. Phys. Chem.* **78**, 639 (1979).
- ¹³R. Weiler, R. Bose, and P. B. Macedo, *J. Chem. Phys.* **53**, 1258 (1970); A. Dietzel and H. P. Poegel *Proceedings of the 3rd International Glass Congr., Venice*, 319, 1963.
- ¹⁴L. M. Torell, *J. Chem. Phys.* **76**, 3467 (1982); L. M. Torell and R. Aronson, *ibid.* **78**, 1121 (1983); C. A. Angell and L. M. Torell, *ibid.* **78**, 937 (1983).
- ¹⁵R. M. Lynden-Bell, M. Ferrario, I. R. McDonald, and E. Salje *J. Phys. Condens. Matter* **1**, 6523 (1989).
- ¹⁶S. Nosé, *J. Chem. Phys.* **81**, 298 (1984).
- ¹⁷G. P. Johari and M. Goldstein, *J. Chem. Phys.* **55**, 4245 (1971); M. Goldstein, *J. Chem. Phys.* **51**, 3728 (1969).
- ¹⁸J.-L. Barrat, W. Götze, and A. Latz, *J. Phys. Condensed Matter* **1**, 7163 (1989).
- ¹⁹E. N. Ivanov, *Sov. Phys.* **18**, 1041 (1964); *J. Exptl. Theor. Phys. (USSR)* **45**, 1509 (1963).
- ²⁰J. H. R. Clarke and S. Miller, *Chem. Phys. Lett.* **13**, 97 (1972).
- ²¹P. J. Carrol and G. D. Patterson, *J. Chem. Phys.* **82**, 9 (1985).
- ²²L.-T. Cheng, Y.-X. Yan and K. A. Nelson, *J. Chem. Phys.* **91**, 6052 (1989).