

Fast rotational reorientation of NO_3^- ions and its relation to the glass transition in $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ liquid: A ^{15}N NMR spin-lattice-relaxation study

S. Sen

Department of Physics, University of Wales, Aberystwyth, SY23 3BZ, United Kingdom

J. F. Stebbins

Department of Geological and Environmental Sciences, Stanford University, Stanford, California 94305

(Received 9 February 1998; revised manuscript received 30 April 1998)

The fast reorientational dynamics of the NO_3^- ions in the supercooled $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ (CKN) liquid have been investigated in the temperature range $370\text{ K} \leq T \leq 440\text{ K}$ by ^{15}N NMR spin-lattice-relaxation spectroscopy. The spin-lattice relaxation of the ^{15}N nuclides is shown to be controlled by the spin rotation process. The correlation time τ_c of the rapid reorientational dynamics of the NO_3^- ions associated with spin rotation is found to be strongly decoupled from the shear/structural relaxation time scale in this temperature range, varying from $10^{-11.8}\text{ s}$ at 370 K to $10^{-12.5}\text{ s}$ at 440 K . An anomalous bifurcation in τ_c into a slow and a fast branch is observed at $T \leq 365\text{ K}$ and is found to be intimately related to the appearance of a bimodal spatial heterogeneity in the overall reorientation or tumbling dynamics of the NO_3^- ions in the supercooled CKN liquid near glass transition. In spite of the large decoupling in the time scale, the fast rotational reorientation is shown to be intimately related to the slow tumbling dynamics, resulting in a two-step decay of the orientational correlation of the NO_3^- ions. The results are found to be compatible with the predictions of the mode coupling theory and offer significant physical insight into the hierarchical nature of the dynamics associated with glass transition. [S0163-1829(98)05637-9]

I. INTRODUCTION

The experimental observation of the wide ranging length scales as well as time scales associated with various dynamic processes in a glass-forming liquid plays a key role in our current theoretical understanding of the problem of glass transition. In this respect the fragile glass formers have been the most informative as various dynamic relaxation processes in these liquids are often clearly identifiable and show widely different degrees of coupling between one another with changing temperature.¹ The ionic dynamics in such a model fragile system $\text{Ca}_{0.4}\text{K}_{0.6}(\text{NO}_3)_{1.4}$ (CKN) have been studied in detail with a number of spectroscopic and scattering techniques.² However, only recently, our ^{15}N static nuclear magnetic resonance (NMR) line shape studies have shown conclusively that the overall reorientation or isotropic tumbling dynamics of the NO_3^- planar triangular ions in CKN are closely related to the shear or α -relaxation process near its calorimetric glass transition ($T_g = 333\text{ K}$).³ The time scale of this tumbling process was found to correspond well with the bulk shear relaxation time τ_{shear} , over five orders of magnitude.³ More intriguingly, the NO_3^- tumbling dynamics were found to become bimodally heterogeneous at $T \leq 365\text{ K}$ with the coexistence of a slow- and a fast-tumbling NO_3^- ion population within the temperature range of $340 \leq T \leq 365\text{ K}$. The time scales of the fast- and the slow-tumbling dynamics were found to differ by about an order of magnitude with the former being similar to the τ_{shear} of the liquid.³ Such a dynamical heterogeneity was suggested to be indicative of a spatial distribution of domains of slow- and fast-tumbling NO_3^- ions in the CKN liquid. The physical nature of these slow and fast domains were not clear al-

though they were tentatively assigned to the appearance of "solid-like" and "liquid-like" regions respectively, in the supercooled liquid in this temperature range.³ The temperature of the first appearance of this dynamical heterogeneity on cooling ($T = 365\text{ K}$) corresponds well with the mode coupling transition temperature of CKN ($T_c = 368 \pm 5\text{ K}$) as obtained from recent neutron scattering studies.⁴ A knowledge of the exact physical nature of these "solid-like" and "liquid-like" regions is thus, critical in order to correlate well-characterized dynamical processes in a supercooled liquid with the physical predictions of the mode coupling theory of glass transition. The coexisting slow- and fast-tumbling NO_3^- ions in these regions were found to be characterized by slow and fast ^{15}N spin-lattice relaxation rates respectively.³ Therefore, an understanding of the ^{15}N spin-lattice relaxation mechanism in CKN above T_g and its relation to the observed tumbling dynamics of the $^{15}\text{NO}_3^-$ ions may be of central importance in deciphering the nature of these "solid-like" and "liquid-like" regions.

In this article we report the observation of the fast rotational dynamics of the $^{15}\text{NO}_3^-$ ions in the supercooled CKN liquid by ^{15}N NMR spin-lattice relaxation spectroscopy within the temperature range of $370\text{ K} \leq T \leq 440\text{ K}$ and establish its relationship with the slow NO_3^- tumbling dynamics. The physical significance of these results is discussed in the framework of the mode coupling theory.

II. EXPERIMENTAL DETAILS

A. Sample preparation

The CKN glass was prepared from Isotec reagent grade 99% ^{15}N -enriched KNO_3 and $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ which were

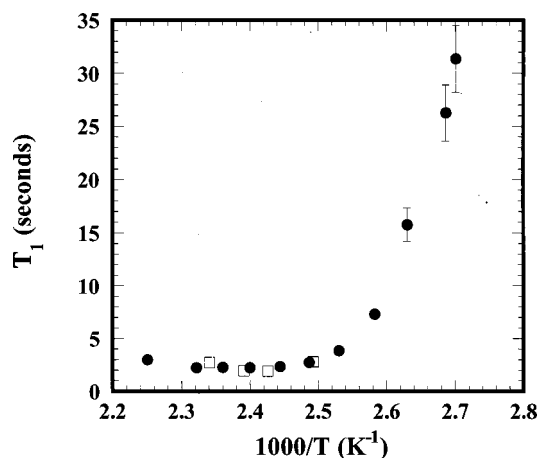


FIG. 1. Temperature dependence of the ^{15}N spin-lattice-relaxation time T_1 (filled circles) in the isotopically enriched supercooled CKN liquid. T_1 data from experiments on a sample with natural isotopic abundance are shown as open squares.

dehydrated at 150 °C in a drying oven until no further weight loss occurred. A stoichiometric mixture of the salts was melted in a pyrex beaker on a hot plate. The liquid was quenched in air after melting for one hour, by pouring it in a pyrex tube at room temperature. The pyrex tube containing the CKN glass was then connected to a high vacuum line and the glass was remelted in vacuum at 533 K in a vertical tube furnace. The pyrex tube was sealed under vacuum followed by quenching of the CKN liquid in air in order to ensure dryness of the sample.

B. NMR spin-lattice-relaxation spectroscopy

The spin-lattice relaxation time (T_1) measurements were carried out under static conditions using the standard saturation-recovery method with a modified Varian horizontal solenoid probe and a modified Varian VXR-400S spectrometer operating at a resonance frequency of 40.54 MHz for ^{15}N .⁵ Following saturation the recovered magnetizations were measured as a function of waiting time from the areas under the fully averaged Lorentzian ^{15}N peaks. Spin-lattice relaxation data could not be obtained at $T < 370$ K as the ^{15}N T_1 's were found to be too long to avoid crystallization of the liquid within the time scale of the measurements.

III. RESULTS AND DISCUSSION

A. ^{15}N spin-lattice-relaxation mechanism in CKN

The ^{15}N T_1 is found to decrease monotonically with increasing temperature from 31.4 s at 370 K to 3.0 s at 440 K (Fig. 1). The spin-lattice relaxation mechanism of the ^{15}N nuclides in CKN liquid may contain contributions from three processes, (i) chemical shift anisotropy (CSA) fluctuation, (ii) dipolar coupling (dd) fluctuation, and (iii) the spin-rotation (SR) process.⁶ Therefore, the experimentally measured T_1 can be expressed as⁶

$$\frac{1}{T_1} = \frac{1}{T_{1(\text{CSA})}} + \frac{1}{T_{1(\text{dd})}} + \frac{1}{T_{1(\text{SR})}}. \quad (1)$$

Previous studies of ^{15}N spin-lattice relaxation of NO_3^- ions in various ^{15}N -enriched aqueous inorganic nitrate solutions have shown that the spin-rotation process is the dominant relaxation mechanism for the $^{15}\text{NO}_3^-$ ions at $T \geq 273$ K whereas the CSA and the dipolar fluctuation processes become important only at lower temperatures.⁶ Moreover, the dipole-dipole interaction was found to be significant for ^{15}N only in the presence of ^1H nuclides in these aqueous systems. In the case of 99% ^{15}N -enriched CKN liquid the low natural abundances and gyromagnetic ratios of all other nuclides ensure that the only significant dipole-dipole interaction is expected to be between the ^{15}N nuclides themselves. T_1 measurements were therefore carried out on natural isotopic abundance CKN liquid where the low abundance (0.38%) of ^{15}N nuclides precluded the possibility of any significant ^{15}N - ^{15}N dipolar coupling. The similar T_1 values for the two liquids (Fig. 1) conclusively show that the dipolar coupling fluctuation is not important in causing ^{15}N spin-lattice relaxation in CKN.

Previous studies have shown that the D_{3h} symmetry of the $^{15}\text{NO}_3^-$ ion results in a uniaxial shielding tensor for ^{15}N nuclides with CSA, $\Delta\sigma \approx 9.5$ kHz in CKN.³ In the case when the spin-lattice relaxation is controlled by the CSA fluctuation due to the reorientation of the NO_3^- ions, the correlation time for such a process τ_{CSA} can be calculated from the experimental T_1 data using the relationship⁷

$$\frac{1}{T_1} = \frac{2}{15} [\omega_L (\Delta\sigma)^2] \tau_{\text{CSA}}, \quad (2)$$

where ω_L is the ^{15}N Larmor frequency. Such calculations yield τ_{CSA} values that are 1 to 2 orders of magnitude slower than τ_{shear} in the temperature range of T_1 measurement. This observation indicates that the ^{15}N spin-lattice relaxation in CKN in this temperature range is not likely to be governed by the CSA fluctuation process. Therefore it can be safely concluded that the spin-rotation interaction is the dominant mechanism of relaxation of ^{15}N nuclides in this temperature range and $1/T_1 \approx 1/T_{1(\text{SR})}$.

B. Determination of correlation times for rotational reorientation of the NO_3^- ions

The spin-rotation interaction is controlled by the coupling between the nuclear spin of a nuclide in a molecule and the angular momentum of the molecule associated with its rapid rotation. In the case of a symmetric rotor such as the NO_3^- ion, the relationship between its rotational angular momentum correlation time τ_J and the spin-lattice relaxation time T_1 due to spin-rotation interaction can be expressed as^{6,8}

$$\frac{1}{T_1} = \frac{2}{3} \frac{\Theta k_B T \bar{c}^2 \tau_J}{\hbar^2}, \quad (3)$$

where Θ is the moment of inertia of the $^{15}\text{NO}_3^-$ ion, \bar{c} is the effective spin-rotation coupling constant, T denotes the absolute temperature, and k_B and \hbar are Boltzmann's and Planck's constants, respectively. The value of \bar{c} for the $^{15}\text{NO}_3^-$ ions in CKN has been approximated to be the same as that (10.7 kHz) determined experimentally for these ions in concentrated aqueous $\text{Ca}(\text{NO}_3)_2$ solution.⁶ The value of Θ has been

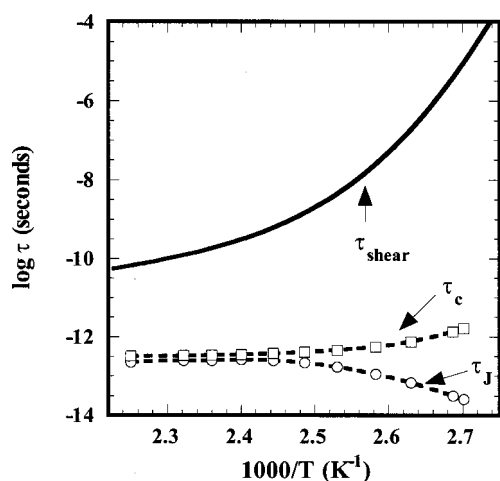


FIG. 2. Temperature dependence of the correlation times τ_J and τ_c for the NO_3^- ions as obtained from the ^{15}N T_1 data using Eqs. (3) and (4), respectively (see text for details). The dashed lines through the data points are guides to the eye only. Note the increasing decoupling of τ_c from τ_{shear} on cooling.

taken to be the same as the theoretical moment of inertia of the $^{15}\text{NO}_3^-$ ion, 9×10^{-46} kg m^2 .⁶ However, it should be kept in mind that such an approximation may not be entirely valid in the case of cooperative rotation of a few $^{15}\text{NO}_3^-$ ions as a cluster in the liquid in which case the effective value of Θ will increase. The angular momentum correlation time τ_J for the ions can then be readily calculated as a function of temperature from Eq. (3) and is found to show a monotonic increase with increasing temperature from $10^{-13.6}$ s at 370 K to $10^{-12.6}$ s at 440 K (Fig. 2).

Previous ^{15}N NMR line shape and quasielastic neutron scattering studies indicate that the fast rotation of the $^{15}\text{NO}_3^-$ ions in CKN is likely to be around the C_3 axis.^{3,9} The reorientational correlation time τ_c of a vector in the plane perpendicular to the axis of rotation, i.e., the NO_3^- plane, can be calculated from τ_J using various diffusion models.^{7,8,10} The time taken by a free $^{15}\text{NO}_3^-$ rotor to reorient by 1 radian, $\tau_F = (\Theta/k_B T)^{1/2}$ is $\approx 10^{-12.4}$ s within our temperature range of T_1 measurement. A comparison between the τ_J values and τ_F shows that at the lowest temperatures of T_1 measurement $\tau_J/\tau_F \ll 1$ and a Debye model of diffusion would be appropriate for calculating τ_c from τ_J . However, at the highest temperatures $\tau_J \approx \tau_F$ and Gordon's extended diffusion model must be employed.⁸ Previous optical Kerr effect (OKE) and Raman scattering studies of the reorientational correlation time scale of the NO_3^- ions in CKN have shown that it is 1 to 5 orders of magnitude shorter with respect to τ_{shear} within the present temperature range.^{11,12} The loss in reorientational correlation is caused by molecular collisions. Thus τ_c is closely related to the average time between the successive collisions experienced by the molecules. As the overall reorientation/tumbling time scale of the NO_3^- ions closely corresponds to τ_{shear} , it can be safely assumed that within the temperature range of T_1 measurements the orientation of the axes of rapid rotation of NO_3^- ions remains fixed in space for a time that is long compared to the time between their successive collisions. In the case of this "one-dimensional rotor" approximation for a symmetric rotor such as the

NO_3^- ion, both the Debye model and the extended diffusion model yield similar results for the relationship between τ_c and τ_J in the temperature range where $\tau_J/\tau_F \ll 1$.⁸ Therefore, we have used the extended diffusion model over the entire temperature range of T_1 measurement in order to calculate τ_c from τ_J . The one-dimensional symmetric rotor approximation for this model yields⁸

$$\tau_c = \tau_J K / (1 - K), \quad (4)$$

where

$$K = (2/\pi)^{1/2} (1/\omega^*) \int_0^\infty \frac{\exp(-\omega^2/2\omega^{*2})}{1 + 4\omega^2\tau_J^2} d\omega.$$

In this expression, ω is the magnitude of the angular velocity vector and $\omega^* = (kT/\Theta)^{1/2}$.

The values of τ_c calculated from Eq. (4) are found to decrease from $10^{-11.8}$ s at 370 K to $10^{-12.5}$ s at 440 K (Fig. 2). The nearly Arrhenius temperature dependence of τ_c (Fig. 2) yields an activation energy of 13 ± 1 kJ mol^{-1} for the NO_3^- reorientational dynamics within this temperature range. This value is in good agreement with the previous Raman scattering results on CKN which yielded a value of 12.5 ± 0.5 kJ mol^{-1} for the NO_3^- reorientational dynamics over a wide temperature range.¹² The numerical values of τ_c obtained in this study are within 1 to 1.5 log units of the NO_3^- reorientational correlation times measured directly using the OKE and Raman scattering techniques, over the same temperature range.^{11,12} Such an agreement is remarkable considering the possible discrepancies that may arise from the approximations regarding the choice of \bar{c} and Θ values in our calculation of τ_J as well as the specific model dependence of the relationship between τ_c and τ_J .

C. Physical nature of the spatial dynamical heterogeneities in CKN liquid at $T \leq 365$ K

Previous studies have shown that the coexisting fast- and slow-tumbling NO_3^- ions in CKN within the temperature range $340 \text{ K} \leq T \leq 365 \text{ K}$ are characterized by short and long T_1 's, respectively.³ It is clear from Eq. (3) that in order for the NO_3^- ions with different T_1 's to coexist at the same temperature, the τ_J and/or Θ of these ions would have to be different. If the slow tumbling NO_3^- ions are rotating as small clusters in a cooperative fashion in the liquid then the effective Θ would be larger than that for a single ion. However, everything remaining the same, an increase in Θ would result in a shorter T_1 for the slow tumbling ions which is in contrary to our observation. Therefore, the slow-tumbling ions with long T_1 's are bound to have a shorter τ_J or, equivalently a longer τ_c , with respect to that for the fast-tumbling ions. Such a difference in τ_J may arise from microscopic spatial heterogeneity in viscosity η in the CKN liquid, as would be predicted by the Stokes-Einstein relationship, $\tau_J = \Theta/8\pi r^3 \eta$ where r is the hydrodynamic radius for the NO_3^- ion.¹⁰ This relationship should be regarded as only approximate in the framework of the extended diffusion model; nevertheless it provides an idea of the physical controlling factors of τ_J in a liquid. Hence, the coexistence of slow tumbling nitrate ions with longer T_1 and fast tumbling

nitrate ions with shorter T_1 in CKN could be associated with the presence of “solid-like” regions with high viscosity and “liquid-like” regions with low viscosity. The close correspondence of the fast-tumbling time scale with τ_{shear} indicates that the bulk viscosity of the supercooled CKN liquid is being controlled by flow in the low-viscosity regions within the temperature range $340 \text{ K} \leq T \leq 365 \text{ K}$.³ The appearance of a solid-like behavior in the density correlation function in a supercooled liquid at the transition temperature T_c is also qualitatively predicted by the mode coupling theory of glass transition.¹³ The physical signature of such a behavior is however, not well known. The close correspondence between the temperature of the first appearance of high- and low-viscosity regions in CKN (365 K) and the mode coupling T_c ($368 \pm 5 \text{ K}$) strongly indicates an association between the predicted solid-like behavior of the density correlation function and the slow dynamics in the high-viscosity regions.

D. Identification of the rotational reorientation of NO_3^- ions with the mode coupling β process

The mode coupling theory predicts the presence of a fast β -process which governs the initial part of a two-step decay of the density correlation function.¹³ Our ^{15}N NMR line shape and spin-lattice relaxation results, when combined, also indicate a two-component decay of the orientational correlation of NO_3^- ions in CKN. The fast ($\approx 10^{-12} \text{ s}$) component corresponds with the rapid rotation of the NO_3^- ions about the C_3 axis; the corresponding reorientational correlation decays due to molecular collisions. The second component represents the considerably slower overall reorientation/tumbling of these ions which randomizes the orientation of the C_3 axis and corresponds with the τ_{shear} of CKN. It is therefore tempting to identify the rapid rotation of the NO_3^- ions with the mode coupling β -process and the tumbling of these ions with the mode coupling α -process. This is supported by the fact that reorientational correlation times τ_c as measured in this study correspond, within 1 to 1.5 log units, with the time scale of the β -process (τ_β) in CKN as measured in previous light scattering studies.¹⁴

The spin-rotation mechanism of ^{15}N spin-lattice relaxation predicts a close relationship between T_1 and τ_c as discussed above. The appearance of a bimodal heterogeneity in the $^{15}\text{N} T_1$ in CKN at $T \leq T_c$ is thus, indicative of a corresponding anomalous bifurcation of τ_c at the same temperature. An anomaly in the β -process at $T = T_c$ is also predicted by the mode coupling theory although it uniquely predicts an increase in τ_β on approaching T_c from both above and below.¹³ Unfortunately, as mentioned before, we could not measure T_1 (and therefore τ_c) below T_c in this study due to crystallization problems in order to verify such a prediction. However, an upper limit on the T_1 of the fast-tumbling component in CKN can be obtained from a ^{15}N differential relaxation experiment carried out in a previous study at $T = 361 \text{ K}$ where the coexisting slow- and fast-tumbling NO_3^- components are best resolved in the ^{15}N line shape.³ Two ^{15}N spectra collected at this temperature with delays of 10 s

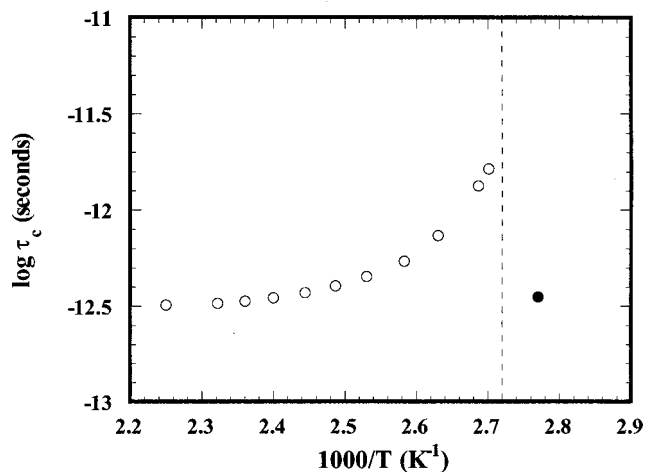


FIG. 3. The variation of τ_c with temperature in the supercooled CKN liquid showing the presence of a cusp at $T \approx 365 \text{ K}$ (dashed line). The value of τ_c at the lowest temperature (filled circle) should be considered as an upper limit only.

and 500 s following the complete saturation of the magnetization shows that the fast-tumbling component has a shorter T_1 with respect to the slow-tumbling one and is fully relaxed in the spectrum collected with 10 s delay.³ Therefore, the T_1 of the fast-tumbling component has to be less than 10 s which imposes an upper limit on the corresponding τ_c value of $\approx 10^{-12.4} \text{ s}$. This limiting value of τ_c obtained at $T = 361 \text{ K}$, when combined with the τ_c values calculated from the T_1 data at $T \geq 370 \text{ K}$, shows the predicted cusp as a function of temperature near the mode coupling T_c (Fig. 3). This observation lends strong support in favor of the existence of a mode coupling β -process and its identification with the rapid rotational reorientation dynamics of the NO_3^- ions in CKN.

IV. SUMMARY

In summary, the ^{15}N spin-lattice relaxation in the supercooled CKN is shown to result from the rapid picosecond time scale rotational reorientation of the NO_3^- ions. This fast reorientational dynamics can be identified with the mode coupling β process in contrast with the α process of slow overall reorientation/tumbling of these ions. These two dynamical processes with widely different time scales are found to be closely interrelated resulting in a two-step decay of the orientational correlation function of the NO_3^- ions. The CKN liquid is shown to become spatially heterogeneous on cooling below the mode coupling T_c with coexisting high- and low-viscosity domains.

ACKNOWLEDGMENTS

The authors acknowledge funding from the Center for Materials Research at Stanford University, supported by the National Science Foundation.

- ¹M. D. Ediger, C. A. Angell, and S. R. Nagel, *J. Phys. Chem.* **100**, 13 200 (1996).
- ²See A. Pimenov, R. Lunkenheimer, H. Rall, R. Kohlhaas, A. Loidl, and R. Böhmer, *Phys. Rev. E* **54**, 676 (1996) and references therein.
- ³S. Sen and J. F. Stebbins, *Phys. Rev. Lett.* **78**, 3495 (1997).
- ⁴E. Kartini, M. F. Collins, B. Collier, F. Mezei, and E. C. Svensson, *Phys. Rev. B* **54**, 6292 (1996).
- ⁵E. Fukushima and S. B. Roeder, *Experimental Pulse NMR: A Nuts and Bolts Approach* (Addison-Wesley, Reading, MA, 1981).
- ⁶T. Saluvere and E. Lippmaa, *Chem. Phys. Lett.* **7**, 545 (1970).
- ⁷H. W. Spiess, in *Dynamic NMR Spectroscopy: NMR, Basic Principles and Progress* (Springer-Verlag, Berlin, 1978), Vol. 15, p. 55.
- ⁸H. W. Spiess, D. Schweitzer, and U. Haeberlen, *J. Magn. Reson.* **9**, 444 (1973).
- ⁹T. Kamiyama, K. Shibata, K. Suzuki, and Y. Nakamura, *J. Non-Cryst. Solids* **192&193**, 272 (1995).
- ¹⁰R. E. D. McClung, *J. Chem. Phys.* **51**, 3842 (1969).
- ¹¹M. Ricci, P. Foggi, R. Righini, and R. Torre, *J. Chem. Phys.* **98**, 4892 (1993).
- ¹²P. Jacobsson, L. Börjesson, A. K. Hassan, and L. M. Torell, *J. Non-Cryst. Solids* **172-174**, 161 (1994).
- ¹³W. Götze and L. Sjögren, *Rep. Prog. Phys.* **55**, 241 (1992).
- ¹⁴G. Li, W. M. Du, X. K. Chen, H. Z. Cummins, and N. J. Tao, *Phys. Rev. A* **45**, 3867 (1992).