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Analysis of the susceptibility minimum observed in $0.4\mathrm{Ca(NO_3)_2}-0.6\mathrm{KNO_3}$ by dielectric spectroscopy and light scattering

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An intriguing feature of the relaxation of glass formers is the broad minimum in the dynamic susceptibility spectrum, lying intermediate between the high frequency vibrational absorption (or Boson peak) and the slower, temperature-dependent structural relaxation and diffusion. As first shown by Lunkenheimer *et al.* [Phys. Rev. Lett. **77**, 318 (1996)], high frequency dielectric spectra can be accounted for by invoking a temperature-dependent, frequency-independent contribution (''constant loss'') to the loss spectrum. Herein, we analyze dielectric relaxation and light scattering data for $0.4\mathrm{Ca(NO_3)_2}$–$0.6\mathrm{KNO_3}$ (CKN), which exhibit broad minima at GHz to THz frequencies. Over a wide temperature range, the spectra can be accurately described by the additive superposition of a constant loss to the structural relaxation and the Boson peak. Moreover, the temperature dependence of the constant loss term is the same for the two spectroscopies. The behavior of the constant loss inferred from this analysis is minimally affected by the details of the fitting procedure, demonstrating the robustness of the method. We also show that dielectric relaxation data for a silver iodide–silver selenate glass conform to the predictions of mode coupling theory, even though a liquid state theory is not obviously applicable to a glassy ionic conductor. This underscores the value of alternative interpretations of the high frequency dynamics in glass-forming liquid, including contributions from a constant loss such as described herein. © *2000 American Institute of Physics.* [S0021-9606(00)70311-4]

I. INTRODUCTION

The susceptibility spectra of glass formers in the 0.1 GHz to 1 THz region, obtained using neutron scattering, light scattering, and high frequency dielectric relaxation techniques, show the presence of a fast relaxation, giving rise to a minimum. The properties of this minimum are often analyzed using the idealized or asymptotic mode coupling theory (aMCT),[1] which predicts a two-step time correlation function, consisting of a fast β process (not to be confused with the secondary β relaxation) and a slow α process. Agreement has been found in fragile glass formers like $0.4\mathrm{Ca(NO_3)_2}$–$0.6\mathrm{KNO_3}$ (CKN)[2–5] and ortho-terphenyl (OTP).[1] Recently, light scattering[6–8] and neutron scattering[6,9] measurements revealed that the fast relaxations of CKN and OTP at temperatures below the aMCT critical temperature, T_c, do not conform to the theory. Also, the dielectric susceptibility minimum at $T<T_c$ for CKN[3–5] (for which T_c is estimated to be 375 K[2]) cannot be explained by mode coupling theory, a point which will be further illustrated in this work.

As an alternative, the dielectric susceptibility minimum at $T>T_c$ can be explained[3–5] by interpreting the fast relaxation in the dielectric spectra as a constant, or nearly constant, dielectric loss.[10–25] The existence of this constant loss has been confirmed in CKN at temperatures below T_c and in many other ionic glass formers at temperatures below their glass transition temperatures, T_g.[26]

Another problem concerning the origin of the fast relaxation according to aMCT is seen in recent light scattering results of Monaco *et al.*[27,28] They found that the fast relaxation process of OTP is present not only in the glassy and supercooled liquid states, but in the crystalline state as well. This observation led Monaco *et al.*[28] to conclude that this fast relaxation is an internal vibrational relaxation, identifiable with neither the fast β relaxation of MCT nor the structural relaxation of the glass transition. On the other hand, the properties of the constant loss indicate that its physical origin may be the anharmonic potential governing the vibrational motions present in glasses, liquids, and crystals.[26]

These developments suggest that, for temperatures both below and above T_c, the fast relaxation may not originate from the β relaxation of aMCT, but from another source, such as the constant loss or internal vibrational relaxation. In this work, we examine this possibility by analyzing the susceptibility spectra of CKN obtained by light scattering,[2] in the manner done for dielectric relaxation;[3–5,26] that is, by assuming that the fast relaxation arises from the constant loss. Our purpose is to determine whether features in both light scattering and dielectric relaxation spectra can be ascribed to a constant loss mechanism, having the same temperature and frequency dependences for both experimental techniques.

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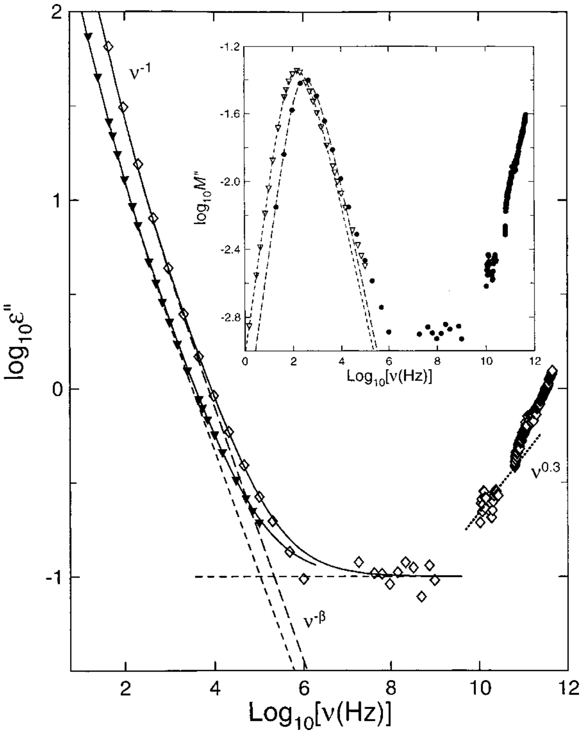

FIG. 1. Imaginary part of the dielectric permittivity versus frequency for CKN at 342 K (◇) from Lunkenheimer *et al.* (Refs. 3,4) and at 342.8 K (▼) from Howell *et al.* (Ref. 33) at 342.75 K. The solid lines represents the sum of a constant loss (horizontal dashed line) and $\varepsilon''(\nu)$ (dashed lines with frequency dependence of ν^{-1} at low frequencies and slope $\nu^{-\beta}$ at high frequencies) calculated from the best fit to the same data in the $M''(\nu)$ representation by the Kohlrausch electric field relaxation function. In the inset, the dashed lines represents the fits of the electrical loss modulus of Lunkenheimer *et al.* (●) and of Howell *et al.* (▽) using the imaginary part of the Fourier transform of the time derivative of the Kohlrausch function with $\beta=0.67$ and $\beta=0.65$, respectively.

II. EVIDENCE FOR THE "CONSTANT LOSS" FROM DIELECTRIC SPECTROSCOPY

Consideraton of the constant dielectric loss has usually been for glassy ionic conductors. Early experimental measurements of the real part of the ac conductivity, $\sigma'(\nu)$, in the easily accessible frequency range of $1<\nu<10^6$ Hz, show that at sufficiently low temperatures $\sigma'(\nu)$ has a frequency dependence of $\nu^{1.0}$. Wong and Angell[10] interpolated between these data and the far infrared lattice absorption data of $Na_2O-3SiO_2$ and suggested that the $\nu^{1.0}$ dependence of $\sigma(\nu)$ at low temperatures will continue to hold at higher frequencies, eventually merging with the low frequency slope of the vibrational absorption peak. This idea was verified up to 2 GHz by measurements on $Na_2O-3SiO_2$ by Burns *et al.*[13] Since then, high frequency results for other glassy ionic conductors indicate a $\nu^{1.0}$ dependence of $\sigma(\nu)$, which persists through the GHz range and beyond. However, in some glasses at higher frequencies ($\omega\equiv 2\pi\nu>10^{10}$ rad/s), the frequency dependence of $\sigma(\nu)$ becomes superlinear, ν^{δ} with $1.3>\delta>1.0$, over a limited frequency range,[18,21,23,24] before being subsumed by the vibrational absorption. The $\nu^{1.0}$ and ν^{δ} dependences of $\sigma(\nu)$ correspond to a constant loss, $\varepsilon''(\nu)=\Delta\varepsilon''$, and to $\varepsilon''(\nu)\propto\nu^{\delta-1}$, respectively. These are consequences of the Maxwell relation, $\sigma'(\nu)=2\pi\nu\varepsilon_0\varepsilon''(\nu)$, where ε_0 is the permittivity of free space. The contribution corresponding to the constant loss has also been observed by nuclear spin-lattice relaxation.[14,29–32]

The origin of the constant loss, which extends from indefinitely low frequencies up to ca. 10 GHz, and the subsequent rise of $\varepsilon''(\nu)\propto\nu^{\delta-1}$ are of great interest, because of their ubiquitous presence in a variety of glassy, crystalline, and molten ionic conductors, including CKN and $0.4Ca(NO_3)_2-0.6RbNO_3$ (CRN). This was brought out in a recent work,[26] which described many examples of ionic conductors having a constant loss contribution in their susceptibility spectra. The magnitude of the constant loss, $\Delta\varepsilon$, and its dependence on both temperature and mobile ion concentration show general features. Except for CKN and CRN, the constant loss contribution in ionic conductors has been determined directly only in the solid state (glassy or crystalline), where over a limited range the temperature dependence of $\Delta\varepsilon''$ is either a power law T^{α} or $\exp(T/T_a)$.

CKN has a small decoupling index R_{τ}, defined as the base 10 logarithm of the ratio of the structural and conductivity relaxation times at the glass temperature $T_g=333$ K.[33] For this reason, the dc conductivity in CKN is comparatively low, whereby the constant loss can be seen directly even above T_g. We illustrate this in Fig. 1, showing the 342 K data (open diamonds) of Lunkenheimer *et al.*[3–5] It is evident that over three decades of frequency, $\varepsilon''(\nu)$ is constant within experimental error. A similar feature is found in the data of Howell *et al.*[33] at 342.75 K (filled inverted triangles in Fig. 1). As is standard practice,[25,33] we fit the imaginary part, $M''(\nu)$, of the electric modulus, $M^*(\nu)\equiv(1/\varepsilon^*(\nu))$, with the imaginary part of the Fourier transform of the time derivative of the Kohlrausch stretched exponential function,

$$\phi(t)=\exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \tag{1}$$

which accounts for the dynamics of the mobile ions. These fits to the data for 342 K of Lunkenheimer *et al.*[3,4] (filled circles) with $\beta=0.67$, and for the 342.75 K data of Howell *et al.*[33] (open inverted triangles) with $\beta=0.65$ are shown in the inset to Fig. 1. The fits describes the two sets of data near the peaks, but underestimate $M''(\nu)$ in the high frequency wing.

The dielectric loss, calculated from $\varepsilon''_{\beta}(\nu)$, is shown as the dashed lines in Fig. 1. At high frequencies, they exhibit a power law dependence

$$\varepsilon''_{\beta}(\nu)\propto\nu^{-\beta}. \tag{2}$$

The solid lines, representing the sum of $\varepsilon''_{\beta}(\nu)$ and a constant loss $\Delta\varepsilon''=0.1$, fit the data well up to 1 GHz; however, the rise of $\varepsilon''(\nu)$ above 10 GHz requires an additional term. The dotted line drawn through the data points with a slope of 0.3 is meant to suggest the possibility that ε'' varies as a power law $\nu^{0.3}$ in a limited region above approximately 10 GHz in CKN, as well as other ionic glass formers.[18,21,23,24] At higher frequencies, there is a more rapid rise due to vibration absorption. Possibly, the $\nu^{0.3}$-dependence is not an additional mechanism, but the result of summing over the constant loss and the low frequency wing of the damped vibrational ab-

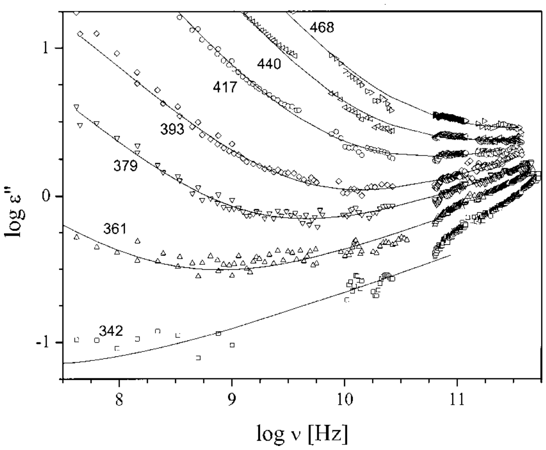

FIG. 2. Dielectric loss for CKN from Lunkenheimer *et al.* (Refs. 3–5) at the indicated temperatures (in Kelvin). The curves are the best fit using Eq. (4).

sorption. We explore these possibilities in the next section, in our analyses of susceptibility spectra obtained by dielectric relaxation and dynamic light scattering.

III. A PARALLEL ANALYSIS OF CKN DIELECTRIC AND LIGHT SCATTERING DATA

All $\varepsilon''(\nu)$ data at temperatures below 361 K show a *broad* minimum, consistent with the presence of a fast relaxation, identifiable with the constant loss. The presence of this constant loss in the dielectric spectra is unambiguous; it extends over three decades in frequency at 342 K, and even further at lower temperatures. There is no reason to expect the abrupt disappearance of the constant loss mechanism at temperatures above 361 K. Therefore, we think that the constant loss mechanism could be responsible for the susceptibility minimum observed at temperatures both above and below T_c. We can examine this possibility by analyzing the susceptibility data of CKN from dielectric relaxation and light scattering measurements in several ways.

A. Method (a)

The dielectric loss data of Lunkenheimer *et al.*[3–5] for CKN at various temperatures are replotted in Fig. 2. These authors fit the $\varepsilon''(\nu)$-minimum using

$$\varepsilon''(\nu)=c_\beta \nu^{-\beta}+\Delta\varepsilon''+c_1\nu, \tag{3}$$

where the first term on the right-hand side represents the high frequency wing of the conductivity relaxation of mobile ions [*viz.*, Eq. (2)], and the last term in Eq. (3) is used to describe the rise due to the far-infrared (FIR) absorption band. As shown by Lunkenheimer *et al.* (see Fig. 3 of Ref. 4), this equation fits the data well for $T \geqslant 379\,\mathrm{K}$. However, at 342 K, the fit is not as good above 10 GHz, due to the power law rise ($\nu^{0.3}$) of $\varepsilon''(\nu)$, as discussed in the previous section. This feature is unaccounted for by Eq. (3), which nevertheless gives both a good fit and a determination of $\Delta\varepsilon''$. The temperature dependence of $\Delta\varepsilon''$ reported by Lunkenheimer *et al.* is presented in the inset to Fig. 3. Also included in the inset is the constant loss at lower temperatures, as deduced from dielectric data of other workers.[26,33,34] There is a rapid rise of $\Delta\varepsilon''(T)$ with T above $T_g=333\,\mathrm{K}$, from approximately 10^{-2} to a value of about 2 at 468 K. This temperature dependence for $\Delta\varepsilon''(T)$ is approximately the same as $\langle r^2(T)\rangle$,[26] the effective mean-square displacement of the ions determined from elastic neutron scattering.[35]

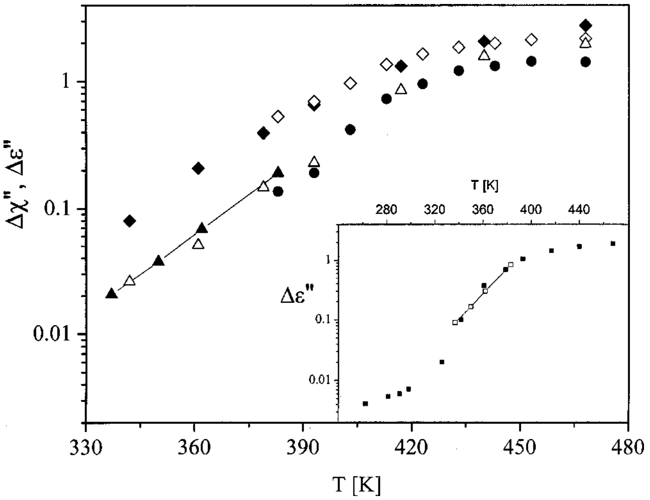

FIG. 3. The temperature dependence of the constant loss determined for CKN. In the inset, $\Delta\varepsilon''$ from Lunkenheimer *et al.* (Refs. 3,4) (solid squared) obtained from the best fit using Eq. (3), and $\chi''(\nu)$ at 0.7 GHz (open squares), from the light scattering spectra determined by Gapinski *et al.* (Ref. 6) scaled by a numerical factor. The main figure shows $\Delta\varepsilon''$ from the best fit of the dielectric spectra using Eq. (4) (open triangles), $\Delta\chi''$ from the best fit of the light scattering spectra of Li *et al.* (Ref. 2) using Eq. (5) scaled by a constant (solid circles), $\Delta\varepsilon''$ from the best fit of the dielectric spectra using Eq. (6) (open diamonds), $\Delta\chi''$ from the best fit of the light scattering spectra using Eq. (7) scaled by a constant (solid diamonds), and $\chi''(\nu)$ at 0.7 GHz from Gapinski *et al.* (Ref. 6) scaled by a numerical factor (solid triangles).

The data of $\varepsilon''(\nu)$ at $T=361\,\mathrm{K}$[3–5] do not exhibit the ''knee'' predicted by *a*MCT. We observe that the frequency dependence of $\varepsilon''(\nu)$ at $T=361\,\mathrm{K}$ is approximately described by a power law $\varepsilon''(\nu)\propto\nu^{0.3}$ from high frequencies down to about 5 GHz, then leveling off at lower frequencies to form a minimum around 1 GHz. This behavior is similar to $\chi''(\nu)$ obtained by Gapinski *et al.*[6] from light scattering at $T=362\,\mathrm{K}$, which shows a power law $\chi''(\nu)\propto\nu^{0.4}$ and the tendency to level off at lower frequencies over the common frequency range down to about 2 GHz. The similarity continues to hold at lower temperatures. These remarkably similar properties of dielectric and light (neutron) scattering spectra for CKN indicate that at temperatures below $T_c \approx 375\,\mathrm{K}$ the susceptibility minima observed in all spectroscopies originate from the same process. That is, they appear to be caused by mechanisms related to the constant loss (e.g., vibrational relaxation), rather than the knee-shaped fast β relaxation of the asymptotic MCT.

From the light scattering susceptibility spectra obtained recently by Gapinski *et al.*,[6] we determine the values of $\chi''(\nu)$ at $\nu=0.7$ GHz for four temperatures below the $T_c \approx 385\,\mathrm{K}$ of *a*MCT. These are plotted (as open squares in Fig. 3 inset) after scaling by a constant. Apparently, the temperature dependence of $\chi''(\nu)$ at $\nu=0.7$ GHz is nearly the same as that of $\Delta\varepsilon''(T)$, indicating once more that the same fast relaxation is probed by light scattering and dielectric relaxation.

B. Method (b)

As discussed above, the crossover of the constant loss to $\varepsilon''(\nu) \propto \nu^{\gamma}$ with $\gamma \approx 0.3$ must be included to better fit the susceptibility spectra for temperature below about 379 K. This behavior is similar to that found in the high frequency dielectric spectra of glassy ionic glass formers. In fact, for some glassy ionic conductors at high frequencies, the $\nu^{1.0}$ dependence of $\sigma(\nu)$ (i.e., ε''=constant) becomes a superlinear frequency dependence $\nu^{\gamma+1}$ (i.e., $\varepsilon'' \propto \nu^{\gamma}$ with $0.2 < \gamma < 0.3$) over a limited frequency range,[18,21,23,24] before a rapid rise to the vibrational absorption peak. Therefore, a better phenomenological description of the $\varepsilon''(\nu)$ minimum of CKN requires incorporation of a crossover from constant loss to power law behavior, prior to the rapid rise to the FIR absorption peak. This is possible by substituting in Eq. (3) the term $c_3\nu^{0.3}$ for $c\nu$, similar to the previous work by others in fitting susceptibility spectra of glycerol and propylene carbonate[36,37]

$$\varepsilon''(\nu) = c_\beta \nu^{-\beta} + \Delta\varepsilon'' + c_3\nu^{0.3}. \tag{4}$$

Following this procedure, we repeat the fit to the dielectric CKN data, obtaining the curves shown (as solid lines) in Fig. 2. The magnitudes deduced for the constant loss are plotted (open triangles) against temperature in Fig. 3. Given the difference between Eqs. (3) and (4), naturally the determinations for the constant loss differ, with Eq. (4) yielding smaller values. However, $\Delta\varepsilon''$ for the two methods have approximately the same variation with temperature, which, moreover, is in agreement with the temperature dependence of $\chi''(\nu)$ at ν=0.7 GHz seen in the light scattering data of Gapinski *et al.*[6] (solid triangles). Therefore, although the choice of ansatz to analyze the dielectric spectra affects the magnitude of the constant loss, the temperature dependence is essentially unchanged.

We have shown the similarities in temperature dependence and frequency dispersion of the light scattering data of Gapinski *et al.*[6] and the dielectric relaxation data of Lunkenheimer *et al.*[3–5] at $T < T_c$. These results, together with the ability to fit the dielectric spectra by the constant loss, means that the light scattering $\chi''(\nu)$ data of CKN for $T < T_c$ should also be satisfactorily accounted for by an equation analogous to Eq. (3).

Depolarized light scattering measurements on CKN were published by Li *et al.*[2] We limit our analysis to the spectra obtained at $T > T_c$, where the data were unaffected by the instrumental artifact,[8] and a minimum is observed in the χ'' spectra. The equation, which is analogous to that used to fit the dielectric spectra (Fig. 4), is

$$\chi''(\nu) = c_\beta \nu^{-\beta} + \Delta\chi'' + c_3\nu^{0.3}, \tag{5}$$

in which $\Delta\chi''$ is a constant, the first term represents the contribution of the high frequency tail of the structural relaxation ($\beta < 1$), and the last term describes the initial rise of the susceptibility prior to the rapid rise on the low frequency wing of the Boson peak. The last term is phenomenological, but its presence is suggested by light scattering measurements at lower temperatures.[6,7]

The fits to the data of Li *et al.* using Eq. (5) are shown in Fig. 4 (thick solid lines). The agreement is satisfactory, although the contribution from the constant loss apparently does not extend to frequencies lower than those associated with structural relaxation. This apparent interplay of vibrational relaxation and structural relaxation should be of interest for the understanding of the constant loss, but is outside the scope of the present work. The constant loss $\Delta\chi''$ deduced from the fits is included in Fig. 3 (solid circles), after multiplication by a constant factor. (The constant factor has no physical meaning because the susceptibility spectra are given in arbitrary units.) It can be seen in this figure that the temperature dependence of $\Delta\chi''$ is very similar to that of $\Delta\varepsilon''(T)$, the latter obtained from fitting the dielectric spectra in a similar fashion [i.e., by Eq. (4)]. Of course, the temperature dependence of $\Delta\chi''$ is closer to that of $\Delta\varepsilon''$ obtained using the similar Eq. (4) than from Eq. (3). The different procedures correspond to different definitions of the constant loss.

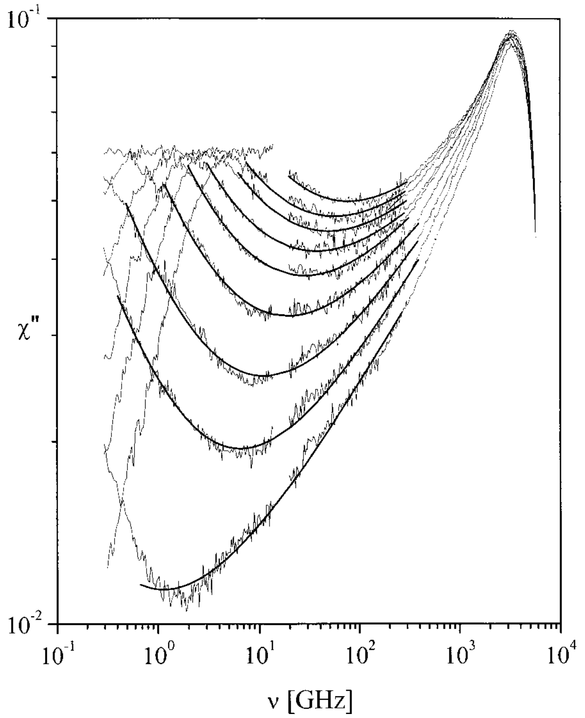

FIG. 4. Light scattering spectra of CKN from Li *et al.* (Ref. 2) (thin lines), along with the fits (thick lines) using Eq. (5). The temperatures, increasing from bottom to top, are 383, 393, 403, 413, 423, 433, 443, 453, and 486 K.

C. Method (c)

We emphasize that the use of Eqs. (4) or (5) is not necessarily the only analysis based on a constant loss that can give a good description of the susceptibility minimum. A constant and its crossover to a frequency dependence of ν^{γ} with $\gamma \approx 0.3$ can also be modeled by a single term $\Delta\varepsilon''(1+\nu\tau_1)^{0.3}$. Hence, viable alternatives to Eqs. (4) and (5) include

$$\varepsilon''(\nu) = \chi_\beta \nu^{-\beta} + \Delta\varepsilon''(1+\nu\tau_1)^{0.3}, \tag{6}$$

and

$$\chi''(\nu) = c_\beta \nu^{-\beta} + \Delta\chi''(1+\nu\tau_2)^{0.3}. \tag{7}$$

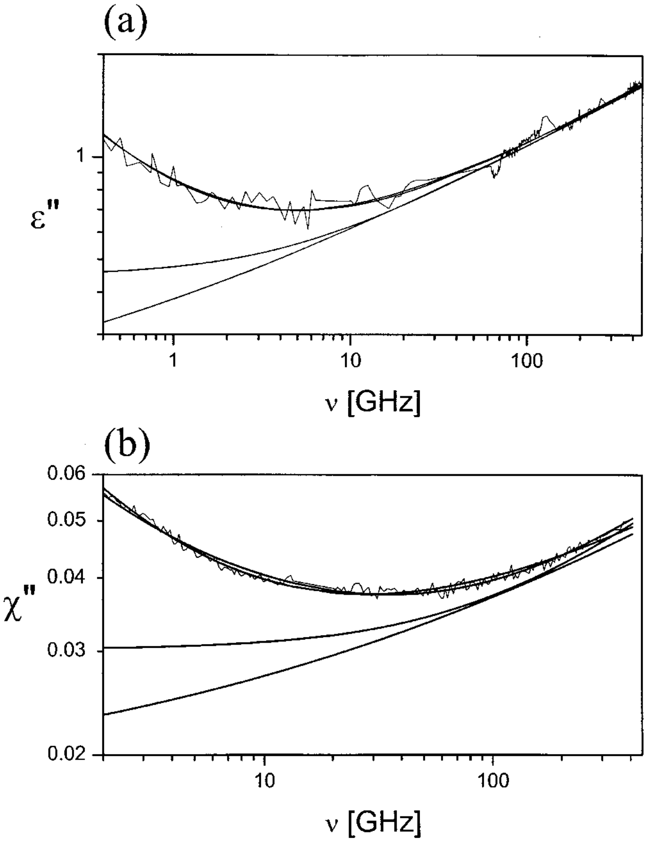

FIG. 5. Comparison of the methods to estimate the constant loss. (a) Imaginary part of the dielectric permittivity, ε'', versus frequency for CKN measured at $T=379$ K from Lunkenheimer *et al.* (Refs. 3,4) (thin line), best fits obtained by using Eqs. (4) and (6) (solid and dotted thick lines, respectively), best fits obtained by using Eqs. (4) and (6) but without the contribution of the term $c_\beta\nu^{-\beta}$ (lower and middle lines, respectively). (b) Imaginary part of the susceptibility, χ'', versus frequency for CKN measured at 423 K from Li *et al.* (Ref. 2) (thin line), best fits obtained using Eqs. (5) and (7) (solid and dotted thick lines, respectively), best fits obtained using Eqs. (5) and (7) but without the contribution of the term $c_\beta\nu^{-\beta}$ (lower and middle lines, respectively).

These equations are similar to Eqs. (4) and (5), differing only by a crossover to a power law, rather than a simple sum of the two terms. Included in Fig. 3 are the $\Delta\varepsilon''$ and $\Delta\chi''$ obtained by fits of dielectric and light scattering data using Eqs. (6) and (7), respectively. The two sets of results again show very similar temperature dependences. The different definitions of $\Delta\varepsilon''$ and $\Delta\chi''$ for Eqs. (4) and (5) compared to Eqs. (6) and (7) yield different magnitudes, as illustrated in Figs. 5(a) and 5(b) for $T=379$ and 423 K, respectively.

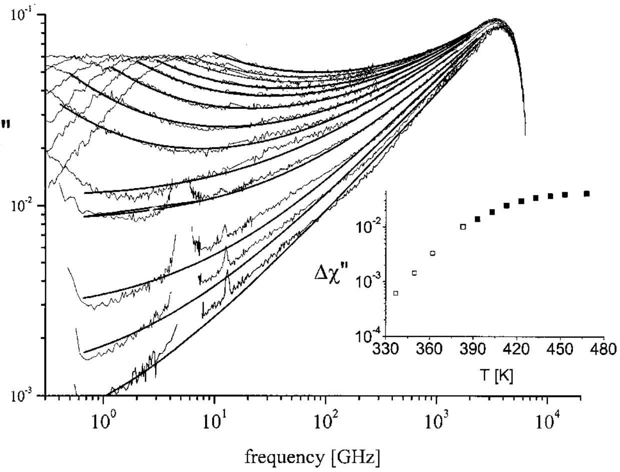

FIG. 6. Light scattering spectra of CKN at (from bottom to top) 337, 350, 362, and 383 K (from Gapinski *et al.* (Ref. 6) after division by a factor of 3500), and at 383, 393, 403, 413, 423, 433, 443, 453, and 468 K [from Li *et al.* (Ref. 2)]. The thicker lines represent the best fits obtained by using Eq. (8). The inset shows the $\Delta\chi''$ deduced from these fits: open squares (Ref. 8), solid squares (Ref. 2), the former again scaled by a numerical factor to yield a continuity between the two data sets. The intersection of the data at 375 K is suggestive of T_c from MCT, albeit derived from an interpretation that is unrelated to MCT.

D. Method (d)

Earlier, we mentioned the possibility that the crossover at higher frequency of $\varepsilon''(\nu)$ from a constant to a power law with exponent ≈ 0.3, prior to the rapid rise to the Boson peak, is just the consequence of adding the low frequency wing of the damped vibrational absorption to the constant loss. We now examine this possibility in dynamic light scattering susceptibility spectra obtained above and below T_c. Light scattering results are more suitable than dielectric relaxation spectra for this purpose, because the entire Boson peak is available for the former. The low frequency wing of the Boson peak in CKN over an appreciable frequency range decreases as a power law ν^B, where B is positive, less than unity, and temperature dependent. We extrapolate this ν^B dependence of χ'' to lower frequencies, assuming that this extrapolation represents the damped Boson peak, which together with the constant loss makes an additive contribution to the susceptibility. This assumption leads us to fit the light scattering susceptibility spectra of Li *et al.*[2] for $T>T_c$ and of Gapinski *et al.*[6] for $T>T_c$ and $T<T_c$ using

$$\chi''(\nu)=c_\beta\nu^{-\beta}+\Delta\chi''+c_B\nu^B. \tag{8}$$

The $c_B\nu^B$ term represents the contribution from the Boson peak. At each temperature, the exponent B and the prefactor c_B are determined from the low frequency flank of the Boson peak; these values are then used in fitting the susceptibility minimum by Eq. (8). Therefore, as far as the constant loss contribution is concerned, Eq. (8) involves no additional parameters byeond those in the previous Eqs. (3)–(7).

The fits to the data, shown in Fig. 6, are satisfactory, extending to much higher frequencies than by the other methods, without the use of additional parameters. The constant loss $\Delta\chi''$ determined from these fits are shown in the inset to Fig. 6 as a function of temperature. The $\Delta\chi''$ obtained from the data of Gapinski *et al.*[6] (open circles) have been scaled by a numerical factor to allow comparison with the data of Li *et al.*[2] (filled circles). Again, the numerical factor has no physical significance because the data are given in arbitrary units. The two sets of results for $\Delta\chi''$ join smoothly, varying with temperature in a similar manner as $\Delta\chi''$ and $\Delta\varepsilon''$ deduced by the other methods (Fig. 3).

The change in slope of the data in the Fig. 6 inset, indicated by the intersection of the slopes of the data points, occurs at 375 K. This would correspond to T_c, suggesting that the seeming ''singularity'' of the MCT nonergodicity parameter at T_c,[1] may be a consequence of the constant loss mechanism. Thus, features present in experimental data that are in agreement with MCT are not necessarily evidence uniquely for MCT. Moreover, we stress that there is no real singularity in the temperature dependence of $\Delta\chi''$ and $\Delta\varepsilon''$ at any temperature, as can be seen in Fig. 6.

IV. MCT ANALYSIS OF THE SUSCEPTIBILITY MINIMUM OF A GLASSY, FAST ION CONDUCTOR

The susceptibility minima in $\varepsilon''(\nu)$ and $\chi''(\nu)$ of CKN and $0.4\mathrm{Ca(NO_3)_2}$–$0.6\mathrm{RbNO_3}$ (CRN) have been analyzed[3–5] according to the precepts of *a*MCT, which predicts the spectral form[1]

$$\varepsilon''(\nu)=\varepsilon''_{\min}[a(\nu/\nu_{\min})^{-b}+b(\nu/\nu_{\min})^{a}]/(a+b), \tag{9}$$

for the minimum at temperatures higher than the MCT critical temperature T_c. In Eq. (9), $\varepsilon''_{\min}(\nu)$ and $\nu_{\min}$ are, respectively, the height and the location of this minimum. The exponents a and b describe the respective high and low frequency wings of the minimum, which are independent of temperature and related to each other via another fit parameter λ by the equations $\lambda=\Gamma^2(1-a)/\Gamma(1-2a)=\Gamma^2(1+b)/\Gamma(1+2b)$, where Γ is the gamma function. The first equation implies that $a<0.4$, and hence a pronounced sublinear increase of $\varepsilon''(\nu)$ at $\nu>\nu_{\min}$. For $T>T_c$, the commonly used version of MCT predicts the following critical temperature dependences:

$$\nu_{\min}\propto(T-T_c)^{1/2a}, \tag{10}$$

$$\chi''_{\min}\propto(T-T_c)^{1/2}, \tag{11}$$

and

$$\tau_\alpha\propto\eta/T\propto(T-T_c)^{-\gamma}, \tag{12}$$

where τ_α is the characteristic time of the α relaxation and $\gamma=(1/2a)+(1/2b)$.

The good agreement of the fits of the CKN dielectric and light scattering minima for $T>T_c$ with $T_c=375\,\mathrm{K}$ by the *a*MCT Eqs. (9)–(12) lends support to the theory.[1] The constant loss explanation of the susceptibility minima offers no predictions concerning the temperature dependence, so in this respect MCT may seem the preferable explanation. However, as we show below, the temperature dependences for the susceptibility minima predicted by MCT are not particularly critical and can in fact be captured by the constant loss mechanism in glassy ionic conductors.

Silver iodide–silver selenate (SISE) with composition $0.48(\mathrm{AgI_2}$–$0.52\,\mathrm{Ag_2SeO_4}$ is a glassy ionic conductor,[21,22] having all the ionic conductivity relaxation properties of CKN and CRN. Because the $\mathrm{Ag^+}$ ion has much greater mobility than the potassium and calcium ions in CKN, the high frequency dielectric susceptibility minima of SISE, similar in every respect to those of the CKN and CRN melts, can be observed within the glassy state. However, since SISE is a glass, MCT should not be relevant to the description of its susceptibility spectra.

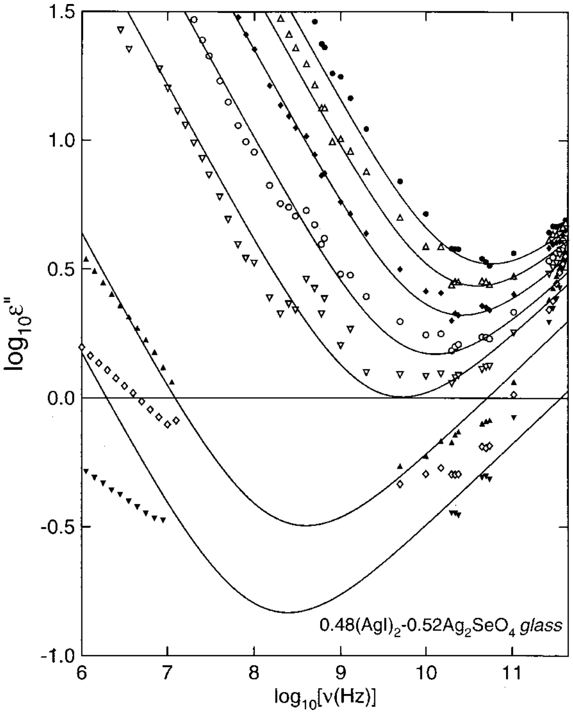

FIG. 7. Frequency dependence of the dielectric loss of a glassy ionic conductor, $0.48(\mathrm{AgI})_2$–$0.52\mathrm{Ag_2SeO_4}$ (SISE), at various temperatures. The solid lines are fits using the MCT expression, Eq. (1), with $\lambda=0.716$ ($a=0.32$ and $b=0.614$).

The frequency dependences of $\varepsilon''(\nu)$, $\sigma'(\nu)$, and $M^*(\nu)$ of SISE, with $\nu_{\max}$ varying over the range $10^2<\nu_{\max}<10^9\,\mathrm{Hz}$, are similar to those of CKN and CRN. We emphasize that the data of SISE are for the high frequency region between 10^6 and $10^{12}\,\mathrm{Hz}$, the same as for CKN and CRN.[1,3–5] Double-logarithmic plots of the dielectric loss $\varepsilon''(\nu)$ of SISE as a function of ν at several temperatures are shown in Fig. 7. We fit $\varepsilon''(\nu)$ by Eq. (9) of MCT with $a=0.32$ and $b=0.614$, corresponding to the exponent $\lambda=0.716$. The fits (Fig. 7) are satisfactory, except at the highest frequencies (above $10^{11.4}\,\mathrm{Hz}$), where the rise is steeper than the MCT fits. The discrepancies in this region increase with decreasing temperature, similar to the MCT description of the CKN dielectric spectra.

Using the obtained $a=0.32$ and $b=0.614$, we can examine the MCT predictions for the temperature dependences of $\nu_{\min}\propto(T-T_c)^{1/2a}$, $\varepsilon''_{\min}\propto(T-T_c)^{1/2}$, and $\nu_{\max}\propto(T-T_c)^{\gamma}$ with $\gamma=(1/2a+1/2b)$. Figures (8a)–(8c) show the results of our fits to the $\varepsilon''_{\min}$, $\nu_{\min}$, and $\nu_{\max}$ data of SISE. In these plots, the ordinate scales are chosen such that the data should fall on a straight line, whose extrapolation yields T_c according to MCT. Indeed, all three sets of data follow the predictions quite well, with a critical temperature $T_c=196\,\mathrm{K}$. The largest deviations are found in Fig. 8(c). The departures of the $\nu_{\max}$ data from the MCT prediction $\nu_{\max}\propto(T-T_c)^{\gamma}$) is understandable because the temperature dependence of $\nu_{\max}$ for the ionic glass SISE is Arrhenius, with sizable activation energy, rather than the power law predicted by the MCT.

The point we are making is that one would not expect MCT, even with inclusion of hopping,[1] to be applicable to the dynamics of ions in a *glass* such as SISE since MCT is an extension of liquid state theories. The susceptibility minima of SISE (Fig. 7) may not be due to the fast β process of the MCT. On the other hand, as for other glassy ionic conductors, the constant loss contribution in SISE at lower

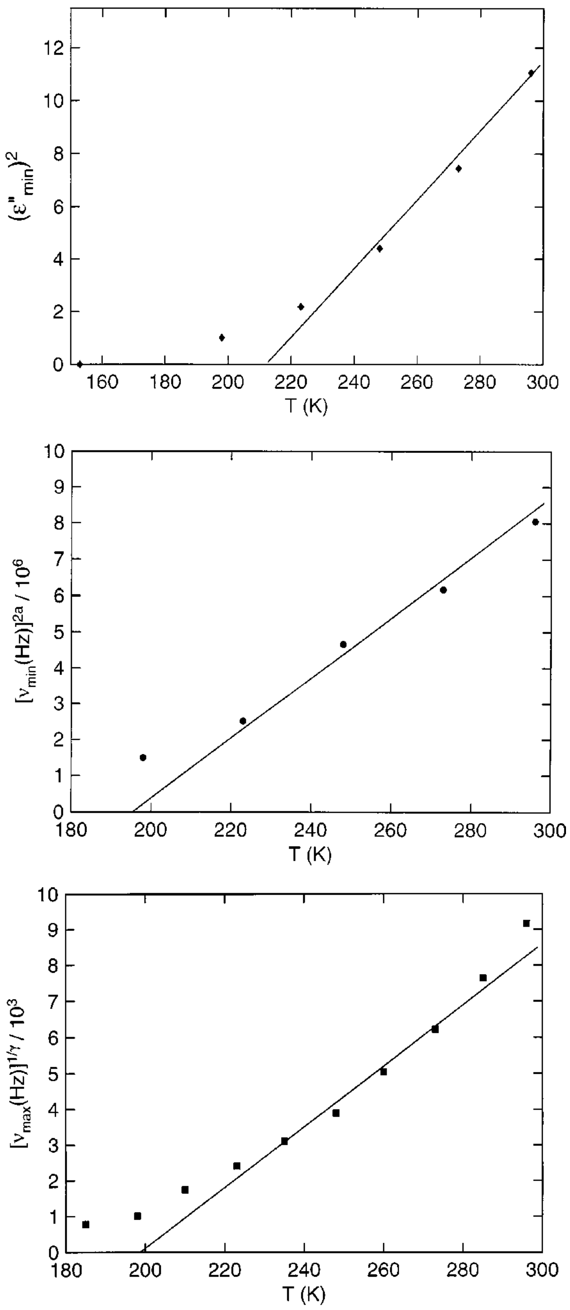

FIG. 8. Temperature dependence of the height and position of the dielectric loss minimum and the α peak (M'' peak) position of $0.48(AgI)_2–0.52Ag_2SeO_4$. The chosen representations should yield straight lines according to the predictions of MCT [Eqs. (2)–(4)]. (a) ε''^2_{min} versus T; (b) $[\nu_{min}(Hz)]^{2a}$ versus T; and (c) $[\nu_{max}(Hz)]^{1/\gamma}$ versus T. The solid lines extrapolate to a T_c of about 196 K for the three quantities.

frequencies, as well as the crossover to $\varepsilon''(\nu) \propto \nu^{\delta-1}$ with $(\delta-1) \approx 0.3$ at higher frequencies in the vicinity of 10^{10} Hz, clearly exists. These contributions can explain the susceptibility minima of SISE, as demonstrated by Lunkenheimer *et al.*[3–5] for CRN and in Fig. 2 herein for CKN by the use of the sum $\Delta\varepsilon'' + c_3\nu^{0.3}$. Nevertheless, the frequency dependence of the susceptibility minima of the SISE *glass* and the temperature dependences of ε''_{min}, ν_{min}, and ν_{max} are in accord with the MCT predictions, Eqs. (9)–(12). This agreement with MCT of the susceptibility minima of ionic *glasses*, which are definitely caused by the constant loss, suggests that the susceptibility minima of glass-forming *liquids* may also be caused by the constant loss, even though they can be described by MCT.[1–5] Thus, an analysis of susceptibility minima in glass-forming liquids showing agreement with MCT does not rule out the constant loss as the actual cause.

V. DISCUSSION

The temperature dependences of the constant loss for CKN determined, respectively, from dielectric relaxation and from the light scattering susceptibility are equivalent, and quite similar to the temperature dependence of the mean-square displacement deduced from the Debye–Waller factor for CKN.[26,35] This similarity of their temperature dependence implies that the constant loss and the mean-square displacement are related. Since the temperature dependence of the mean-square displacement is determined by anharmonicity, it has been suggested that the mechanism of the constant loss is vibrational relaxation caused by the anharmonicity of the potential.[26] Comparable temperature dependences of the fast relaxation have been obtained from the quasielastic light scattering intensity for poly(methylmethacrylate) (PMMA), polycarbonate, and polybutadiene.[38–40] In addition, quasielastic neutron scattering in PMMA and polycarbonate[38] reveals that the magnitude of the fast relaxation is related to the mean-square displacement obtained from the Debye–Waller factor, as found for the constant loss in CKN.[26] This also led to the conclusion[38,39] that the fast process corresponds to overdamped vibrations.

Thus, the constant loss contribution is a viable explanation of the susceptibility minimum. Such a result is timely, since there are recent experimental indications[6–9] that the fast relaxation, certainly below T_c and possibly even above T_c, may not come from the *a*MCT. The observation of the fast relaxation in crystalline, as well as in supercooled, OTP[28] rules out any relationship to MCT, or to glass transition (structural relaxation) phenomenon. Instead, the fast relaxation is likely a vibrational process,[28] a conclusion also reached from the properties of the constant loss.[26]

Although there is direct evidence for the existence of the constant loss at lower temperatures, the physical origin of the constant loss and the closely related fast relaxation in light and neutron scattering spectra remain unknown. The possibility that they result from nonlinear Hamiltonian dynamics of anharmonic vibrations has been suggested.[41] In particular, the relaxation of nonlinear (anharmonic) vibrations in a lattice could well be the fast relaxation observed in the susceptibility spectra.[42] Numerical solution of nonlinear vibrations located at sites interacting linearly with nearest neighbors shows that the vibrational relaxation follows a Kohlrausch stretched exponential time dependence, Eq. (1). With increasing effects from anharmonicity, β decreases and tends to zero. When β is small, the vibrational relaxation contributes a susceptibility that is very slowly varying on a logarithmic frequency scale, resembling the constant loss and the fast process seen in dielectric and light (neutron) scattering experiments. Novikov[43] has also advanced a theory showing that the anharmonicity of vibrations leads to quasielastic scattering in glasses and supercooled liquids.

If the constant loss or vibrational relaxation is responsible for the susceptibility minimum, the question becomes whether there is a theory of the α relaxation that, when combined with the constant loss contribution, can account for the susceptibility spectra at all temperatures. We point out that the coupling model (CM)[44–46] can do just that. While many relaxation models invoke the Kohlrausch function to describe structural relaxation, according to the CM, there is an additional process, referred to as the primitive or fast α relaxation, occurring prior to a crossover time t_c. This primitive process involves independent (noncooperative) motion, described by a relaxation time, τ_0. Kohlrausch behavior is only observed beyond t_c (≈ 2 ps), when structural relaxation begins to be governed by intermolecular cooperativity. For high temperature data at frequencies beyond those considered herein, the CM is able to capture the behavior on the subpicosecond time scale.[47–50] The model has been applied successfully to experimental results on the short-time relaxational dynamics of OTP,[51,52] glycerol,[53,54] methanol,[55] and zinc chloride.[56]

As clear from the results presented herein, the CM alone cannot explain the appearance of the susceptibility minima, as Schneider *et al.*[37] demonstrated from dielectric relaxation spectra, and Cummins from light scattering data.[57] At most measurement temperatures, the fast primitive relaxation of the CM makes a negligible contribution to the observed susceptibility minima. This is because either its contribution is confined to the frequency range of ν greater than 8×10^{10} Hz (which corresponds to $t<t_c\approx 2$ ps), or τ_0 is too long (i.e., $\tau_0 \gg t_c$) such that its contribution is negligible even in the frequency regime $\nu > 8\times 10^{10}$ Hz. Thus, under the conditions of the experimental measurements of CKN, glycerol, and propylene carbonate, only a single slow α-relaxation peak with no fast relaxation is expected. However, in combination with a fast relaxation coming from the constant loss mechanism (i.e., vibrational relaxation), the susceptibility minima may be accounted for by the coupling model, as shown by our fits of dielectric and light scattering susceptibility spectra using any of the methods (a)–(d).

VI. CONCLUSIONS

Independent of the ansatz chosen to model the constant loss, the susceptibility spectra of both light scattering and dielectric relaxation for CKN, below and above T_c, can be well-described by invoking a constant loss mechanism. In combination with the Boson peak and structural relaxation, as modeled for example by the Kohlrausch expression, the constant loss gives rise to extra intensity, which determines the minimum of the susceptibility of CKN, as seen experimentally in the GHz to THz region. While the properties of this minimum are commonly interpreted according to MCT,[1] the present results suggest an alternative explanation. The values for the constant loss extracted from analyses of light scattering and dielectric spectra have the same temperature dependence. Along with its other properties,[26–28] this suggests the constant loss has its origin in anharmonicity of the vibrational motion, which eventually leads to structural relaxation. From the shape of the light scattering spectra at high temperature, it appears that the contribution from the constant loss is either terminated or overwhelmed by the structural relaxation at longer times.

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[1] W. Götze, J. Phys.: Condens. Matter **11**, A1 (1999).

[2] G. Li, W. M. Du, X. K. Chen, H. Z. Cummins, and N. J. Tao, Phys. Rev. A **45**, 3867 (1992); G. Li, M. Fuchs, W. M. Du, A. Latz, N. J. Tao, J. Hernandez, W. Götze, and H. Z. Cummins, J. Non-Cryst. Solids **172–174**, 43 (1994).

[3] P. Lunkenheimer, A. Pimenov, and A. Loidl, Phys. Rev. Lett. **78**, 2995 (1997).

[4] P. Lunkenheimer, A. Pimenov, M. Dressel, B. Gorshunov, U. Schneider, B. Schiener, and A. Loidl, in *Supercooled Liquids, Advances and Novel Applications*, edited by J. T. Fourkas, D. Kivelson, U. Mohanty, and K. A. Nelson, ACS Symposium Series Vol. 676 (1997) 168 (ACS, Washington, DC).

[5] P. Lunkenheimer, A. Pimenov, M. Dressel, B. Gorshunov, U. Schneider, B. Schiener, R. Böhmer, and A. Loidl, in *Structure and Dynamics of Glasses and Glass Formers*, MRS Symposium Proceedings, 455, 47 (Material Research Society, Pittsburgh, 1997).

[6] J. Gapinski, W. Steffen, A. Patkowski, A. P. Sokolov, A. Kisliuk, U. Buchenau, M. Russina, F. Mezei, and H. Schober, J. Chem. Phys. **110**, 2312 (1999).

[7] N. V. Surovtsev, J. Wiedersich, V. N. Novikov, E. Rössler, and A. P. Sokolov, Phys. Rev. B **58**, 14888 (1998).

[8] H. C. Barshilia, G. Li, G. Q. Shen, and H. Z. Cummins, Phys. Rev. E **59**, 5625 (1999).

[9] F. Mezei and M. Russina, J. Phys.: Condens. Matter **11**, A341 (1999).

[10] J. Wong and C. A. Angell, *Glass Structure by Spectroscopy* (Dekker, New York, 1976).

[11] K. L. Ngai, A. K. Jonscher, and C. T. White, Nature (London) **277**, 185 (1979).

[12] K. L. Ngai, R. W. Rendell, and H. Jain, Phys. Rev. B **30**, 2133 (1984).

[13] A. Burns, G. D. Chryssikos, E. Tombari, R. H. Cole, and W. M. Risen, Phys. Chem. Glasses **30**, 264 (1989).

[14] K. L. Ngai, U. Strom, and O. Kanert, Phys. Chem. Glasses **33**, 109 (1992).

[15] U. Strom, K. L. Ngai, and O. Kanert, J. Non-Cryst. Solids **131–133**, 1011 (1991).

[16] W.-K. Lee, J. F. Liu, and A. S. Nowick, Phys. Rev. Lett. **67**, 1559 (1991).

[17] A. S. Nowick, A. V. Vaysleyb, and W. Liu, Solid State Ionics **105**, 121 (1998).

[18] B. Durand, G. Taillades, A. Pradel, M. Ribes, J. C. Badot, and N. Nelhadj-Tahar, J. Non-Cryst. Solids **172–174**, 1306 (1994).

[19] X. Lu and H. Jain, J. Phys. Chem. Solids **55**, 1433 (1994).

[20] K. L. Ngai, H. Jain, and O. Kanert, J. Non-Cryst. Solids **222**, 383 (1997).

[21] C. Cramer and M. Buscher, Solid State Ionics **105**, 109 (1998).

[22] K. L. Ngai, J. Non-Cryst. Solids **248**, 194 (1999).

[23] C. Cramer, K. Funke, and T. Saatkamp, Philos. Mag. B **71**, 701 (1995); C. Cramer and K. Funke, Ber. Bunsenges. Phys. Chem. **96**, 1725 (1992).

[24] K. L. Ngai, C. Cramer, T. Saatkamp, and K. Funke, in *Non-Equilibrium Phenomena in Supercooled Fluids, Glasses and Amorphous Materials*, edited by M. Gordano, D. Leporini, and M. P. Tosi (World Scientific, Singapore, 1996), p. 3.

[25] K. L. Ngai and C. T. Moynihan, Bull. Mater. Res. Soc. **23**(11), 51 (1998).

[26] K. L. Ngai, J. Chem. Phys. **110**, 10576 (1999).

[27] G. Monaco, S. Caponi, R. Di Leonardo, D. Fioretto, and G. Ruocco, Phys. Rev. Lett. **82**, 1776 (1999).

[28] G. Monaco, S. Caponi, R. Di Leonardo, D. Fioretto, and G. Ruocco, Phys. Rev. Lett. (submitted).

[29] J. Szeftel and H. Alloul, J. Non-Cryst. Solids **29**, 253 (1978).
[30] G. Balzer-Jollenbeck, O. Kanert, J. Steinert, and H. Jain, Solid State Commun. **65**, 103 (1988).
[31] O. Kanert, R. Kühler, J. Dieckhöfer, X. Lu, H. Jain, and K. L. Ngai, J. Non-Cryst. Solids **172–174**, 1277 (1991).
[32] W. Franke, Ph.D. thesis, Fachbereich Chemie der Universität Hannover, 1993.
[33] F. S. Howell, R. A. Bose, P. B. Macedo, and C. T. Moynihan, J. Phys. Chem. **78**, 639 (1974).
[34] D. L. Sidebottom, P. F. Green, and R. K. Brow, Phys. Rev. Lett. **74**, 5068 (1995).
[35] E. Kartini, M. F. Collins, B. Collier, F. Mezei, and E. C. Svensson, Phys. Rev. B **54**, 6292 (1996).
[36] P. Lunkenheimer, U. Schneider, R. Brand, and A. Loidl, AIP Conf. Proc. **469**, 433 (1999).
[37] U. Schneider, P. Lunkenheimer, R. Brand, and A. Loidl, Phys. Rev. E **59**, 6924 (1999).
[38] A. Mermet, E. Duval, N. V. Surovtsev, J. F. Jal, A. J. Dianoux, and A. F. Yee, Europhys. Lett. **38**, 515 (1997); E. Duval, A. Mermet, N. V. Surovtsev, and A. J. Dianoux, J. Non-Cryst. Solids **235–237**, 203 (1998); Philos. Mag. B **77**, 457 (1998); and submitted to J. Chem. Phys.
[39] A. P. Sokolov, W. Steffen, and E. Rössler, J. Phys.: Condens. Matter **8**, 9567 (1996); A. P. Sokolov, in Ref. 5, p. 69; J. A. H. Wiedersich, N. V. Surovtsev, V. N. Novikov, E. Rössler, and A. P. Sokolov, Phys. Rev. E (in press).
[40] U. Buchenau, Prog. Theor. Phys. Suppl. **126**, 126 (1997).
[41] K. L. Ngai and C. M. Roland, in Ref. 5, p. 81.
[42] G. P. Tsironis and S. Aubry, Phys. Rev. Lett. **77**, 5225 (1996); A. Bibaki, N. K. Voulgarakis, S. Aubry, and G. P. Tsironis, Phys. Rev. E **59**, 1234 (1999).
[43] V. N. Novikov, Phys. Rev. B **58**, 8367 (1998).
[44] K. L. Ngai, Comments Solid State Phys. **9**, 121 (1979).
[45] K. L. Ngai and R. W. Rendell, in *Supercooled Liquids, Advances and Novel Applications*, edited by J. T. Fourkas ACS Symposium Series 676, 45 (American Chemical Society, Washington, DC, 1997).
[46] K. Y. Tsang and K. L. Ngai, Phys. Rev. E **54**, R3067 (1996); **56**, R17 (1997).
[47] K. L. Ngai, C. M. Roland, and G. N. Greaves, J. Non-Cryst. Solids **182**, 172 (1995).
[48] C. M. Roland and K. L. Ngai, J. Chem. Phys. **103**, 1152 (1995).
[49] C. M. Roland and K. L. Ngai, J. Chem. Phys. **104**, 2967 (1996).
[50] C. M. Roland and K. L. Ngai, J. Chem. Phys. **104**, 8171 (1996).
[51] C. M. Roland, K. L. Ngai, and L. J. Lewis, J. Chem. Phys. **103**, 4632 (1995).
[52] C. M. Roland and K. L. Ngai, J. Time Dep. Mat. **66**, 109 (1997).
[53] K. L. Ngai and C. M. Roland, Phys. Rev. E **55**, 2069 (1997).
[54] C. M. Roland and K. L. Ngai, J. Chem. Phys. **106**, 1187 (1997).
[55] K. L. Ngai and C. M. Roland, J. Phys. Chem. **101**, 4437 (1997).
[56] K. L. Ngai and C. M. Roland, Phys. Rev. E **54**, 6969 (1996).
[57] H. Z. Cummins, G. Li, Y. H. Hwang, G. Q. Shen, W. M. Du, J. Hernandez, and N. J. Tao, Z. Phys. B **103**, 501 (1997).