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Depolarized light scattering spectroscopy of $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$: A reexamination of the ‘‘knee’’

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The ‘‘knee’’ found in the depolarized light scattering spectra of $Ca_{0.4}K_{0.6}(NO_3)_{1.4}$ at low temperatures by G. Li, W.M. Du, X.K. Chen, H.Z. Cummins, and N.J. Tao [Phys. Rev. A **45**, 3867 (1992)] appears to have been an experimental artifact. The origin of this feature is analyzed, and its implications for the mode coupling theory of the liquid-glass transition are considered. [S1063-651X(99)02105-4]

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I. INTRODUCTION

In 1992, a depolarized light scattering (DLS) study of the mixed-salt glass-forming material CKN $[Ca_{0.4}K_{0.6}(NO_3)_{1.4}]$ carried out in our laboratory [1] gave susceptibility spectra $\chi''(\omega)$ exhibiting pronounced minima for temperatures above 110 °C whose shape and temperature dependence were compared with predictions of the idealized mode coupling theory (MCT). For temperatures below 80 °C, a weak downward-concave feature was observed in these spectra at low frequencies (the ‘‘knee’’) which was also compared to MCT predictions. From this analysis, the MCT crossover temperature T_C for CKN was estimated as 378 K (105 °C), a value subsequently confirmed by time-resolved spectroscopy by Yang and Nelson [2]. In Fig. 1 we show the composite intensity spectra $I(\omega)$ from Ref. [1] obtained with a tandem Fabry-Perot interferometer (TFPI) and a Raman spectrometer; in Fig. 2, the $\chi''(\omega)$ spectra obtained from the intensity spectra are shown for (a) temperatures from 110–305 °C, and (b) for temperatures from 23–100 °C, illustrating these two features.

Subsequent DLS studies in our laboratory of the glass-forming materials Salol [3], propylene carbonate [4], glycerol [5], isopropylbenzene [6], and orthoterphenyl [7] revealed susceptibility minima similar to what was found for CKN, but gave no evidence for a knee. Furthermore, for T above but close to T_C, the susceptibility spectra were found to lie systematically above the MCT predictions for all materials studied, including CKN. This deviation was recognized as a manifestation of activated transport (hopping) processes which prevent complete structural arrest at T_C, an effect not included in the original idealized version of MCT used in the first analysis of the CKN and salol spectra.

The CKN and salol DLS data were therefore reanalyzed, using the extended version of MCT which includes a temperature-dependent hopping parameter $\delta(T)$, and these discrepancies were eliminated [8]. The extended MCT was also employed in the analysis of DLS spectra of propylene carbonate [4] and orthoterphenyl [7]. While the hopping effect produces minor qualitative changes for T above T_C, its effects for temperatures below T_C can be dramatic, restoring the minimum and, if sufficiently large, shifting the knee out of the spectral window of DLS measurments [9]. Once the implications of hopping were recognized, the question became: why is the knee observed in CKN since it is not seen in other structural glass-forming materials?

Recently, two groups have reexamined DLS spectra of CKN, and have found that the knee can be eliminated by the addition of a narrow-band dielectric filter to the Fabry-Perot optics [10,11], suggesting that the knee observed in our CKN experiments was an experimental artifact. The authors of Ref. [11] also discussed the possible relevance of this result for the MCT interpretation of the liquid-glass transition, a question we will return to below. We have also reexamined the CKN DLS spectra and found qualitative agreement with the results of these two groups. The sample and experimental procedure were the same as those discribed in Ref. [1] and were also very similar to Refs. [10,11].

II. ORIGIN OF THE SYNTHETIC KNEE

Figure 3 illustrates the principal elements underlying the appearance of the synthetic knee in the $\chi''(\omega)$ spectra. The DLS spectrum of CKN at $T=343$ K (70 °C) is shown at the

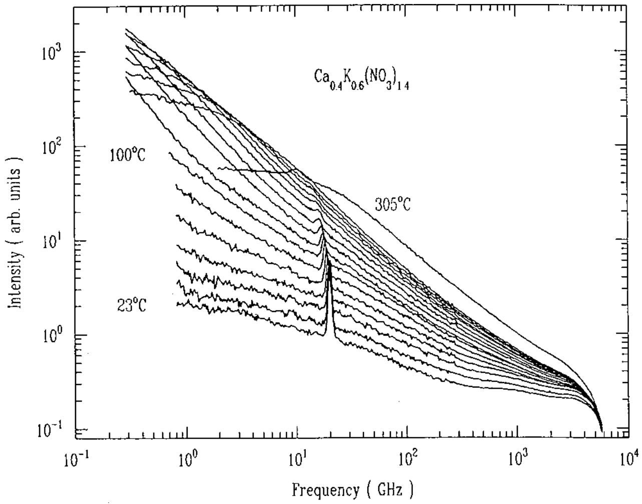

FIG. 1. Composite depolarized $\theta=173°$ light-scattering spectra of CKN for temperatures from 305 °C (top) to 23 °C (bottom). These spectra were collected with the Amici prism plus pinhole filter as described in the text. The sharp lines near 20 GHz are due to leakage of the intense LA Brillouin lines by imperfect polarizers. [From Li *et al.*, Phys. Rev. A **45**, 3867 (1992).]

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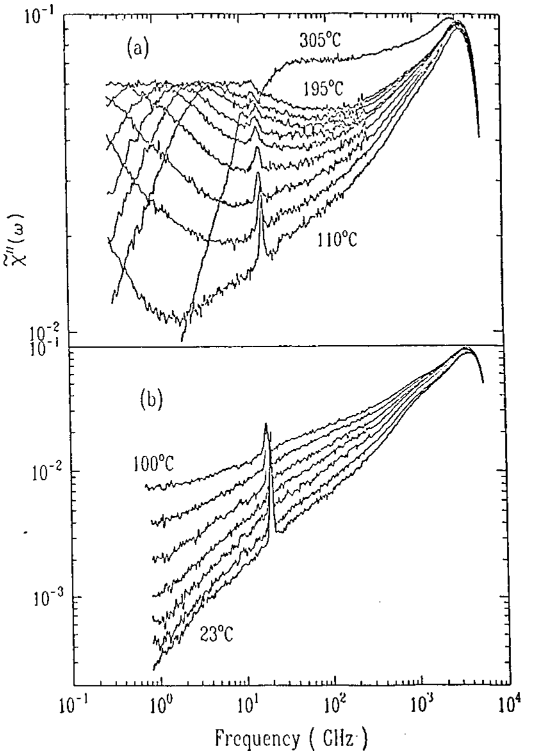

FIG. 2. Susceptibility spectra obtained from the data in Fig. 1 by division by the Bose factor $[n(\omega)+1]$. (a) For temperatures from 110 to 305 °C; (b) for temperatures from 23 to 100 °C. [From Li *et al.*, Phys. Rev. A **45**, 3867 (1992).]

top, on a log-log plot in (a) and on a semilog plot in (b). Beneath it, in (c), are the transmission spectra of the Amici prism plus 0.65 mm pinhole combination used in our original CKN experiment [1] measured with the Raman spectrometer (the pinhole was placed 42 cm from the prism, just as it is in the TFPI), and of the 1 nm bandpass dielectric filter (Oriel Corporation, model 52630) obtained with the TFPI with plate spacing of 0.5 mm. The maximum transmission of the filter is 0.3, while that of the prism is 0.83, a significant difference when working with a weak scatterer such as CKN, which is why we originally chose the prism-pinhole filter for these experiments.

While the Sandercock TFPI effectively suppresses neighboring orders, there is high transmission occurring approximately every 20 orders. (We could not measure this higher-order transmission directly since it exceeds the scan range of our interferometer.) Referring to Fig. 3, there will be signal present when the prism-pinhole combination is used, for higher orders with frequencies up to approximately 6000 GHz. With the smallest plate separation we used (0.5 mm), there will only be two active higher-order transmission maxima, at approximately ±6000 GHz from the central order. From Fig. 3, the combined signal from these two extra transmission maxima should be approximately 5% of that from the central order and can be neglected. For the largest separation (20 mm), however, there will be transmission maxima approximately every 150 GHz, so there will be additional signal from about 40 points on the spectrum, producing a flat background approximately 2.4 times as strong as the desired spectrum scanned by the central order. In practice, the background can be smaller than this theoretical estimate since the higher-order transmission maxima are generally weaker than that of the central order. While the addition of such a flat background does not change the $I(\omega)$ vs f slope on a linear scale, it will increase the slope towards zero on a log-log plot. In Fig. 4, the relative intensities of the spectra obtained with and without the interference filter are shown, with the filter transmission already divided out. If there were no extra intensity, the two spectra should be identical. The ratio of the two, for $d=20$ mm, is approximately

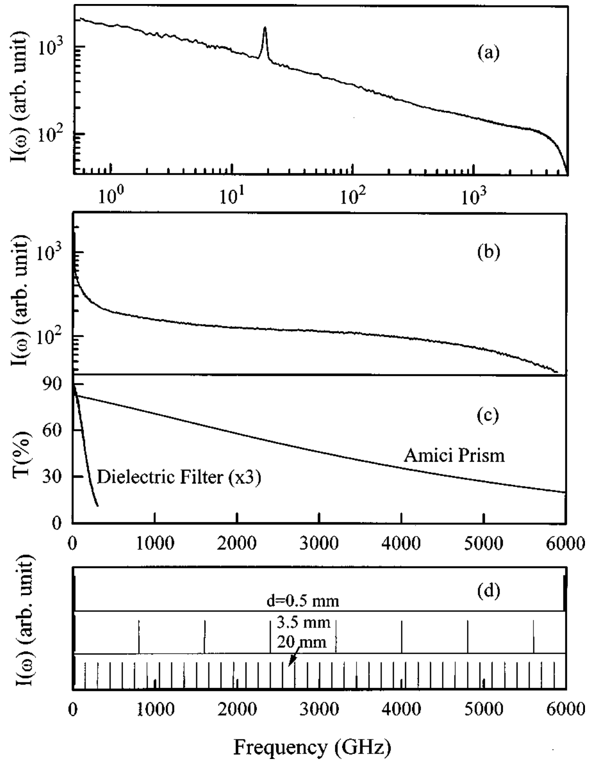

FIG. 3. The intensity spectrum $I(\omega)$ at 70 °C on (a) a log-log plot and (b) a semilog plot. (c) Transmission functions of the Amici prism plus pinhole filter, and of the narrow bandpass dielectric filter. (d) Positions of the $20n$ $(n=1,2,3,\ldots)$ transmission maxima of the TFPI with mirror separations of 0.5, 3.5, and 20 mm.

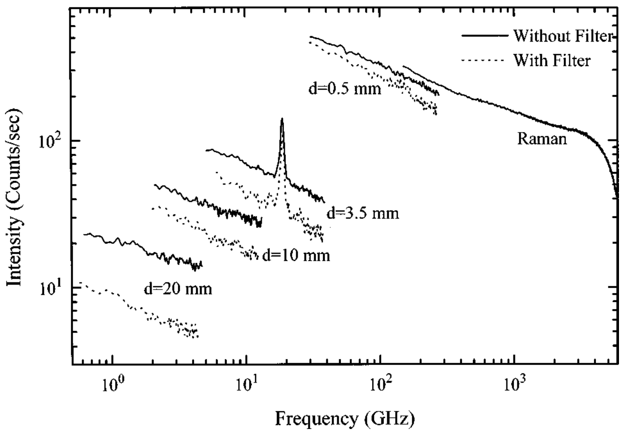

FIG. 4. Intensity spectra obtained at $T=70$ °C with the Raman spectrometer and with the TFPI with four mirror separations. Solid lines: Amici prism plus pinhole filter only. Dotted lines: with 1 nm interference filter added. Each spectrum has been divided by the filter transmission function.

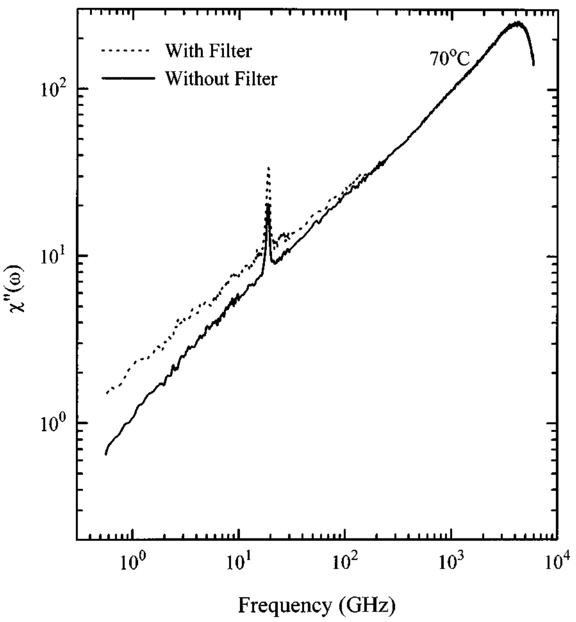

FIG. 5. Composite susceptibility spectra $\chi''(\omega)$ at $T = 70\,°\mathrm{C}$ obtained from the data of Fig. 4. Solid line: without dielectric filter; dotted line: with dielectric filter.

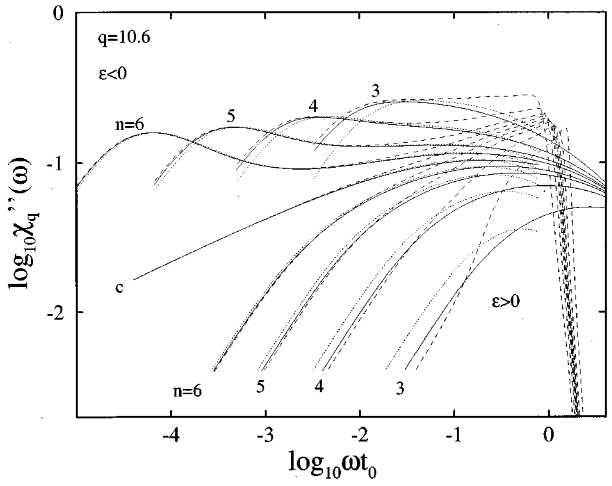

FIG. 6. Susceptibility spectra for the hard-sphere system obtained by numerical solution of the MCT equations. Dashed lines: Newtonian dynamics model. Full lines: Brownian dynamics model. (Dotted lines refer to a discrete dynamics model discussed in the reference.) Decreasing n (for $\epsilon > 0$) indicates states lying deeper in the glass. [From Franosch *et al.*, J. Non-Cryst. Solids **235-237**, 71 (1998).]

2.0, in qualitative agreement with the above estimate.

Consequently, we should expect the addition of the flat background selectively to the large separation spectrum to cause a slope increase at low frequencies on a log-log plot, leading to a synthetic ''knee.'' In Fig. 4 just such an effect can be seen. In Fig. 5, the weak downward bend in the $\ln[\chi''(\omega)]$ vs $\ln[\omega]$ plot at low frequencies for $T = 70\,°\mathrm{C}$ is seen when the prism-pinhole combination is used, but not when the narrow-band interference filter is included, as previously observed by Refs. [10,11]. Furthermore, since the intensity of the low-frequency part of the spectrum decreases with decreasing temperature, this effect extends to higher frequencies as the temperature decreases, so that the apparent ''knee'' moves towards higher frequencies with decreasing temperature, as found in Ref. [1]. Thus, the previously neglected higher-order transmission of the tandem Fabry-Perot interferometer, together with the temperature dependence of the spectral intensity, conspire to produce a kneelike synthetic feature with shape and temperature dependence resembling the predictions of MCT. The CKN ''knee'' reported in Ref. [1], and discussed in several subsequent publications, should therefore be considered as an experimental artifact.

The synthetic knee was not observed with other materials such as salol, glycerol, propylene carbonate, or orthoterphenyl which scatter much more strongly than CKN at low frequencies, presumably due to orientational dynamics. Thus, the weak scattered intensity of CKN at low frequencies relative to the strong high-frequency vibrational intensity explains why the synthetic knee was observed only in this material. We note that while no identifiable ''knee'' was observed in these other materials, a qualitative scaling procedure based on the idealized MCT was attempted for $T < T_C$ for the susceptibility spectra of salol and propylene carbonate. In view of the possibility that these low-temerature spectra may have also been somewhat perturbed by the overlapping order problem, these scaling analyses should also be reexamined.

III. IMPLICATIONS FOR MCT

The observation of a susceptibility minimum and a knee in the CKN spectra by Li *et al.* [1] provided support for the idealized-MCT scenario of the liquid-glass transition. MCT predicts, for temperatures above the MCT crossover temperature T_C, a crossover in the susceptibility spectrum from ω^{-b} to ω^{a} at a scaling frequency ω_σ, which produces a minimum. For $T < T_C$, it predicts a low-frequency crossover from ω^1 to ω^a which should produce a ''knee.'' In colloidal glasses, where the idealized MCT seems to be applicable, the time equivalent of the knee is observed, producing a cusp in the scaling time vs temperature plot [12]. However, it has long since become clear that the knee may not be observable if hopping effects are important, which appears to be the case for all structural glasses studied so far, including CKN.

Other predictions of the MCT were also considered by the authors of Refs. [10,11]. In particular, the slope of the $\chi''(\omega)$ vs ω log-log plots were observed to be temperature dependent, in apparent violation of the MCT prediction of constant slope a. Furthermore, the amplitude of the susceptibility spectra, in this power-law region, was found to decrease with decreasing temperature similarly for neutron scattering and light scattering spectra, again in apparent disagreement with MCT.

In evaluating the significance of these results, it should be recalled that the MCT predictions of constant slope and amplitude are asymptotic predictions, expected to apply only in a limited range of temperatures close to T_C and for frequencies close to the scaling frequency ω_σ. Measurement of the slope over too large a frequency range will inevitably be perturbed by the high-frequency microscopic structure (the boson peak), leading to an a_{eff} unrelated to the critical exponent a of MCT.

Determining the range of applicability of the MCT asymptotic predictions is a major challenge. The first quantitative analysis, for the hard-sphere system, was reported by Franosch *et al.* [13]. A related analysis, of particular relevance for the present discussion, was reported in Ref. [14] and is reproduced in Fig. 6. Susceptibility spectra for the hard-sphere system are shown, computed by numerical solution of the MCT equations both with Newtonian microscopic dynamics (dashed lines) and with Brownian microscopic dynamics (full lines) in which the inertial term is dropped so that the short-time dynamics are relaxational. The lower part of the plot ($\epsilon>0$) refers to the glass state, with n increasing as the critical point (c) is approached. Note that, with increasing distance from the critical point (decreasing n), the dashed lines show an apparent slope increase due to interference from the vibrational dynamics. Note, also, that the amplitude of the curves decreases with increasing distance from the critical point for both models, qualitatively resembling the results reported in Ref. [11], suggesting that this is an intrinsic property of the dynamics and not of the light-scattering mechanism. Since the temperature dependence of the apparent slope and amplitude evident in Fig. 6 result from solutions of the MCT equations, similar temperature dependence observed in experimental data cannot be viewed as inconsistent with MCT.

In conclusion, the knee reported in Ref. [1] appears to have been an experimental artifact, and we therefore withdraw it. However, we believe that the implications of this erroneous identification for the MCT scenario of the liquid-glass transition are minimal, in view of the important role played by activated processes which were not recognized when the CKN knee was first reported.

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