Reply to "Comment on 'Light-scattering investigation of α and β relaxation near the liquid-glass transition of the molecular glass Salol' " and "Reexamination of the depolarized-light scattering spectra of glass-forming liquids"

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The data analysis procedures employed in our previous publications [Phys. Rev. A **45**, 3867 (1992); **46**, 3343 (1992); Phys. Rev. E **47**, 4223 (1993)] are reviewed and the significance of the cusp found in the scaling time τ_β is described. The implications of the Salol dielectric susceptibility results described by Dixon, Menon, and Nagel in their Comment [preceding paper, Phys. Rev. E **50**, 1717 (1994)] are discussed. The relation between the alternative model presented in the Comment by Zeng, Kivelson, and Tarjus [second preceding paper, Phys. Rev. E **50**, 1711 (1994)] and the mode-coupling theory is considered, and their alternative model is shown to be incompatible with experimental results, particularly inelastic neutron-scattering spectroscopy where the dipole-induced-dipole scattering mechanism is inoperative.

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In their Comment [1], Zeng, Kivelson, and Tarjus (ZKT) discuss our depolarized-light-scattering studies of calcium potassium nitrate (CKN) [2] and Salol [3] and present numerous criticisms of the data analysis procedures we used to test the idealized [2,3] and extended [4] mode-coupling theory (MCT) of the liquid-glass transition. We believe that there are serious problems with their Comment, both in its discussion of our data analysis procedures and in its description of the MCT. Before addressing these problems, we will briefy summarize some general aspects of MCT that must be considered in carrying out experimental tests of the theory, and will also consider the Comment of Dixon, Menon, and Nagel (DMN) [5].

The MCT equations used by us and by others to fit experimental data are leading-order asymptotic results, deduced from expansions in the vicinity of the dynamical glass transition singularity (GTS) exhibited by the MCT equations of motion for the density fluctuation modes. These results are obtained for both the temperature separation $|T - T_C|$ and the hopping parameter δ close to zero. The range of validity in $|T - T_C|$ and δ of these asymptotic expansions is not known for the materials we studied. One expects, in analogy to critical phenomena, that corrections to scaling will be required beyond the asymptotic region. Nevertheless, as a first approximation, these asymptotic equations are generally used to analyze experimental data with all coefficients taken as constants, fixed by their values at the crossover temperature T_C.

The idealized MCT whose predictions were tested in [2,3] and in many other experimental studies is a convenient, simplified version of the complete extended theory used in Ref. [4]. The original 1984 MCT glass transition publications [6,7], which included only nonlinear interactions among density fluctuation modes in the memory function, led to the prediction of complete structural arrest (an ergodic-to-nonergodic transition) at T_C. However, as Das and Mazenko [8] pointed out, correction terms ignored in these first publications could effectively cut off the structural arrest. Götze and Sjögren [9,10] then carried out a detailed analysis of the generalized kinetic equations previously developed for simple liquids, and identified the contributions to the memory kernel which provide a first correction to the idealized MCT. They found a new set of closed equations of motion, the extended MCT, which include ergodicity-restoring effects. Calculations for a schematic model with this extended MCT [9] demonstrated the decay of the correlation function at long times, and the persistence of the α peak and susceptibility minimum for temperatures below T_C (see Fig. 2 of Ref. [10]). A detailed analysis of the extended theory for the intermediate β-relaxation regime was presented in Ref. [11]. Since 1987 it has thus been clear that for long times (or low frequencies), at temperatures near or below T_C, the idealized theory should be viewed as a first convenient approximation and that experimental data should also be analyzed with the extended theory which includes an additional parameter, the temperature-dependent hopping rate $\delta(T)$. Nevertheless, experimentalists have generally continued to analyze data with the idealized theory which is simpler and more tractable than the extended theory.

In our publications [2,3], spectra obtained with a tandem Fabry-Pérot interferometer and with a grating spectrometer were combined, and the composite spectra were then converted to susceptibility spectra $\chi''(\omega)$. Initially undertaken to further explore the broad self-similar spectral wing we had observed in CKN [12], the remarkable resemblance of the resulting CKN $\chi''(\omega)$ spectra to the $\chi''(\omega)$ spectra predicted by the MCT (see Fig. 2 of Ref. [2] and Fig. 2 of Ref. [10]) led us to carry out a detailed analysis of our data based on the idealized version of the MCT in order to test various MCT predictions, particularly its scaling predictions.

At temperatures above $\sim 120\,^\circ$C, the CKN $\chi''(\omega)$ spectra exhibit two distinct peaks: a high-frequency (microscopic) peak near 2000 GHz which is relatively independent of temperature, and a lower-frequency strongly-temperature-dependent peak, associated with the primary α-relaxation process, which moves rapidly towards lower frequencies with decreasing temperature, disappearing from our available spectral window [0.3 – 6000 GHz] at $T \sim 110\,^\circ\mathrm{C}$. Between the α peak and the microscopic peak there is a broad susceptibility minimum which, in the MCT, constitutes the β-relaxation region. We note that in the three materials for which both neutron-scattering and light-scattering experiments have been performed to explore this region, CKN [2,13], glycerol [14], and orthoterphenyl [15], susceptibility minima were found in the same spectral region with both techniques.

In their Comment, DMN [5] report that they have measured the dielectric susceptibility $\epsilon''(\omega,T)$ of Salol in the frequency range where we observed a minimum in the light-scattering spectra, but no minimum was seen in $\epsilon''(\omega,T)$. This is an interesting result. We think that its origin lies in the fact that while neutron and light scattering couple to density fluctuations (and also to some extent to orientational dynamics), the dielectric response is determined by the dynamics of orientable dipoles and *not* by density fluctuations, since the dielectric probe couples to density via electrostriction which is *very weak.* Although MCT is a theory of the dynamics of density fluctuations, it had been generally assumed that translation-rotation coupling would be sufficiently strong so that orientational dynamics would follow the dynamics of the density fluctuations. The result of DMN shows that this is apparently not the case for Salol, at least not in the frequency region of the susceptibility minimum.

DMN suggest that the susceptibility minimum seen in the light-scattering data could result from the superposition of the α peak and the microscopic peak. Although it is of course true that there would necessarily be a minimum between these two peaks, the observed magnitude of $\chi''(\omega)$ in the region of the minimum is too big to be accounted for by this simple superposition, as discussed in Ref. [4] [Fig. 1(b)], so this explanation cannot be correct. As emphasized in the MCT literature, it is not the existence of the minimum that is significant, but its strength.

Note that in the extended MCT, the α peak is predicted to evolve smoothly with temperature, with no observable anomaly near T_C. The interesting manifestations of mode-coupling effects observed in the vicinity of the susceptibility minimum would therefore have little effect on the dielectric response function for which the minimum does not occur. It is therefore not unreasonable for DMN to conclude, on the basis of their dielectric data, that there is no convincing evidence for critical slowing down near T_C. As we will discuss in detail later, the critical-slowing-down phenomenon of MCT concerns the temperature dependence of the scaling frequency ω_σ, and this is not accessible to dielectric measurements.

Turning now to the Comment of ZKT, we first consider their criticism of the procedure we used for analyzing the susceptibility minimum and determining the critical exponents a and b of the MCT. The idealized MCT predicts that the $\chi''(\omega)$ spectra close to the minimum should be described approximately by the interpolation equation

$$\chi''(\omega) = \chi''_{\min}[b(\omega/\omega_{\min})^a + a(\omega_{\min}/\omega)^b]/(a+b), \quad (1)$$

with the two exponents $0 < a \leq 0.4$ (the critical exponent) and $0 < b \leq 1$ (the von Schweidler exponent) determined by a single system-dependent exponent parameter λ through

$$\lambda = \Gamma^2(1-a)/\Gamma(1-2a) = \Gamma^2(1+b)\Gamma(1+2b)\,. \quad (2)$$

Note that one *cannot* in general read off the exponents a and b by simply placing a ruler on $\log[\chi''(\omega)]$ vs $\log(\omega)$ curves because the limiting slopes ω^a and ω^{-b} are only reached far from the minimum, where the effects of the microscopic process (at high ω) or hopping effects (at low ω) may interfere. These exponents must be determined by fits to Eq. (1) in the vicinity of the minimum since this is the center of the frequency interval where Eq. (1) should be valid. Equation (1), with the constraint of Eq. (2) for b, is a three-parameter fit that determines the minimum $(\omega_{\min}, \chi''_{\min})$ and the exponent a. Our fits to Eq. (1) for CKN were performed using Eq. (2) to constrain b, and also with both a and b free, with little difference.

Since in these fits a was found to change somewhat with temperature, a global fit was carried out to find an optimum overall fit value of a ($a = 0.27$) in order to test the MCT predictions

$$\chi''_{\min} \propto (T - T_C)^{1/2}, \quad (3a)$$

$$\omega_{\min} \propto (T - T_C)^{1/2a}\,. \quad (3b)$$

Plots of $\omega_{\min}^{2a}$ vs T and $(\chi''_{\min})^2$ vs T were found to exhibit the linear behavior predicted by Eqs. (3); their intercepts provided two of five separate estimates of the crossover temperature, $T_C = (105 \pm 5)\,^\circ\mathrm{C}$, close to an estimate of T_C found previously from neutron-scattering data [16].

ZKT claim that our determination of a and b from fits to Eq. (1) in Refs. [2,3] is not valid since "the agreement between Eq. (1) and the experimental data is far from convincing; see, for instance, the results for CKN ...". The same CKN $\chi''(\omega)$ data were replotted in Fig. 8 of Ref. [4] where it was shown that the theory matches the data within experimental error in a frequency region around the minimum exceeding two decades. The agreement and the evolution of the matching region with temperature are also consistent with figures in the MCT literature in which the asymptotic interpolation formula (1) was compared with full numerical solutions of the MCT equations. We think that any reader interested in checking our figures can easily see that this ZKT criticism is not justified.

ZKT then assert that "the most direct way to determine a and b from the data ... is to plot $\log(\chi''_{\min})$ vs $\log(\omega_{\min})$ ...". In Refs. [2,3] we discussed this procedure and reported that it led to slopes which disagreed with the results of fits to Eq. (1). In Ref. [4] we analyzed the failure of this cross-check in detail (see Fig. 10 and the accompanying discussion in Ref. [4]). For $T > T_C$, the origin of the disagreement is easily seen by examining the MCT scaling equation

$$\chi''(\omega) = h(T)|\sigma|^{1/2}\hat{\chi}^{\lambda}_{-}(\omega/\omega_\sigma), \quad (4)$$

where $\sigma \propto (T_C - T)/T_C$ is the separation parameter,

$\omega_\sigma \propto |\sigma|^{1/2a}$ is the scaling frequency, and $\hat{\chi}_-^\lambda(\omega/\omega_\sigma)$ is a susceptibility master function uniquely determined by the exponent parameter λ. If $h(T)$ is assumed constant, Eq. (4) recovers Eqs. (3), and $a_{\rm eff}$, the slope of $\log(\chi''_{\rm min})$ vs $\log(\omega_{\rm min})$, should be equal to a. But, as shown in Ref. [4], $h(T)$ actually increases linearly with T in a broad temperature range around T_C, so that $(\chi''_{\rm min})$ increases with $|\sigma|$ faster than $|\sigma|^{1/2a}$. Thus the slope $a_{\rm eff}$ should be bigger than a, as we found. A similar result was also found recently for propylene carbonate (PC) where the difference between a and $a_{\rm eff}$ was analyzed quantitatively [17]. For $T < T_C$, the picture is more complicated because of the influence of the activated hopping terms which also modify the form of $\hat{\chi}(\omega)$.

ZKT assert that their method of determing a and b is more direct than our fits to the susceptibility spectra, and that the failure of $a_{\rm eff}$ and $b_{\rm eff}$ so obtained to satisfy Eq. (2) is a serious contradiction of MCT. We respond that the fact that the slope $a_{\rm eff}$ of $\log(\chi''_{\rm min})$ vs $\log(\omega_{\rm min})$ exceeds the value a expected if $h(T)$ is constant demonstrates that this is *not* a direct way to determine the exponents a and b since it requires prior determination of $h(T)$. Fits to Eq. (1), on the contrary, yield a and b at fixed T and are therefore insensitive to the T dependence of $h(T)$.

ZKT point out correctly that fits of experimental data to MCT equations suffer from uncertainties if one does not know the temperature interval or frequency range where the fits are supposed to work. We agree completely, and have specifically considered this problem in Ref. [4]. In Fig. 8 of [4] we determined the range of temperatures and frequencies in which the data scale, independent of theoretical input. This test showed which data should be included in fitting the asymptotic MCT master function (1) to most reliably fix a and b. This procedure also provided the basis for determining the error bars on the exponent parameter λ given in [4]. Additionally we could find the temperature interval within which fits to the idealized MCT could be used to extrapolate quantities such as $\omega_{\rm min}$ beyond the range of validity of that theory, a crucial issue, e.g., for fixing T_C with Eqs. (3). As a byproduct one finds the temperature and frequency region where it becomes necessary to use the full $\delta \neq 0$ MCT instead of its simplified $\delta = 0$ version as discussed in Fig. 9 of Ref. [4]. We consider it unreasonable to ignore this information in judging the applicability of the MCT.

The second problem with the Comment of ZKT concerns the relation of the "knee" to the scaling frequency τ_β^+. For temperatures below $\sim 110\,^\circ$C the α peak and the susceptibility minimum have moved out of our experimental window, and the CKN $\chi''(\omega)$ spectra exhibit a weakly downward concave form (Fig. 2 of Ref. [2]). The idealized MCT predicts that, for $T < T_C$, $\chi''(\omega)$ should exhibit a crossover from $\chi''(\omega) \propto \omega$ to $\chi''(\omega) \propto \omega^a$, producing a downward concave feature (or knee). Because the location of this crossover does not appear very clearly, we did not attempt to find the knee frequency directly. We determined the scaling frequency ω_e by sliding the $\chi''(\omega)$ curves (on a log-log scale) to achieve maximum overlap (see Fig. 10 of Ref. [2]). This scaling procedure produced the scaling frequency $\omega_e(T)$ and its inverse $\tau_\beta^+(T)$. Because of the incomplete crossover which results in a rather small curvature, the scaling frequency obtained this way does include significant uncertainty. Similarly, for the high-T data, we rescaled the $\chi''(\omega)$ spectra to obtain the scaling frequency and its inverse $\tau_\beta^-(T)$. The cusp shown in Fig. 16 of Ref. [2] therefore resulted from rescaling the experimental data shown in Figs. 6 and 10, *not* from a measurement of the location of the knee. We emphasize that this scaling determination is in agreement with the MCT definition of τ_β.

Because the "knee" in the $\chi''(\omega)$ vs ω CKN data is not mathematically well defined, we also replotted the same data as $\chi''(\omega)/\sqrt{\omega}$ vs ω (Ref. [4], Fig. 11) to convert the knee to a mathematically well-defined maximum. ZKT assert that "the knee frequency of CKN ... in Ref. [2] shifts by a factor of 13 between 353 K and 296 K ... whereas in Ref. [5] it shifts by a mere factor of 3 over the same ... range". In fact the *same* CKN data are shown in these two publications. In the first [2], the scaling frequency ω_e was determined by the theory-independent scaling of the data discussed above which resulted in the factor of 13 cited by ZKT. In the second publication (Ref. [4], Fig. 11), we replotted the data as $\chi''(\omega)/\sqrt{\omega}$ vs ω together with idealized MCT fits. It is the maxima *of these fits* that produced the smaller shift noted by ZKT. This difference is one of several well-understood indications that the idealized MCT may be inadequate for certain frequency intervals at temperatures near and below T_C. Figure 11 in [4] was meant to specifically illustrate such features of the MCT. The important point, however, is that for $T < T_C$ the scaling frequency decreases with increasing temperature, in agreement with a crucial prediction of the MCT.

The above discussion applies to the CKN data [2]. A similar analysis was carried out for Salol [3] with similar results. For Salol, however, the knee feature is entirely washed out by hopping effects in the low-frequency range and by complicated microscopic structure in the high-frequency range. Therefore for $T < T_C$ the scaling frequency was found by scaling the data in an intermediate-frequency range well below the microscopic peak onto a MCT $\hat{\chi}_+^\lambda(\omega/\omega_\sigma)$ susceptibility master curve. The determination of τ_β^+ for Salol is therefore less significant than for CKN (as also noted in the Comment of DMN), but still led to a cusp. (Similar results were found recently for PC [17].)

In Refs. [2,3] we noted many of the problems with the idealized MCT fits discussed by ZKT, including the failure of the cross-checks, the fact that the knee does not show clearly, and the occurrence of systematic deviations observed at low frequencies for temperatures near and below T_C. We noted that this disagreement was probably related to hopping processes not included in the simple idealized version of MCT. The discrepancies found in these fits to the idealized MCT and the large frequency window and high signal-to-noise ratio of our data encouraged us to undertake a new analysis of the CKN and Salol $\chi''(\omega)$ data in collaboration with Götze and his co-workers using the extended MCT [4]. The low-frequency deviations observed near and below T_C in the original analysis, the failure of the cross-checks, and the partial (or complete) washing out of the knee were all accounted for in this new analysis which also led to predictions for the behavior of the susceptibility minimum below T_C. (This spectral region is now becoming experimentally accessible [15] and should provide additional stringent tests of the MCT.) We add that this analysis confirmed the determination of T_C, a, and b reported in [2,3] within the idealized MCT. This demonstrated that the idealized MCT is a useful starting point for the interpretation of experimental data.

ZKT discuss our extended MCT analysis, reported in Ref. [4], which they refer to as a "modified mode-coupling theory of glasses." They assert that the simple (i.e., idealized) mode-coupling analysis requires at least eight adjustable parameters, while in the modified (i.e., extended) theory, at least four more adjustable parameters are needed (for a total of at least 12). We will briefly review the extended MCT analysis in order to correctly count the required number of adjustable parameters.

The correlation function $\phi_A(t)$ of a variable A in the intermediate β-relaxation region is given in the MCT by

$$\phi_A(t) = f_A^c + h_A G(t) \ . \tag{5}$$

The corresponding susceptibility $\chi_A''(\omega)$, determined from the Fourier transform of $\phi_A(t)$, is

$$\chi_A''(\omega) = h_A \chi''(\omega). \tag{6}$$

In the extended MCT, the β correlator $G(t)$ obeys a two-parameter scaling law

$$G(t) = g^{\lambda}(t/t_0, \sigma, \delta t_0), \tag{7}$$

where the matching time t_0 is an arbitrary number introduced to make the time t/t_0 and the hopping rate δt_0 dimensionless. (t_0 is not a fit parameter.) The critical nonergodicity parameter f_A^c and the amplitude factor h_A are equilibrium properties that vary smoothly with T. The correlator G, which describes the time dependence of $\phi_A(t)$ and the frequency dependence of $\chi_A''(\omega)$, is the same for all variables A which couple to the density. $G(t)$ is completely determined by the exponent parameter λ and by the temperature-dependent control parameters $\sigma(T)$ and $\delta(T)$. Both the hopping parameter $\delta(T)$ and the separation parameter $\sigma(T)$ are smooth functions of T. While $\delta(T)$ is always positive, $\sigma(T)$ passes through zero at T_C: $\sigma(T_C) = 0$. The function g^λ can be calculated numerically once λ, σ, and δ are specified [11]. In the limit $\delta \to 0$ where hopping terms are neglected, these results reduce to the idealized MCT, and $\chi''(\omega)$ is given by Eq. (4). (ZKT call this simplification the standard MCT.)

Fits of this extended MCT to our CKN and Salol $\chi''(\omega)$ data in Ref. [4] were performed by fixing λ (which determines a and b) and then optimizing the three temperature-dependent parameters $h(T)$, $\sigma(T)$, and $\delta(T)$ at each temperature. We found that in the temperature range $T_C - 40$ K$< T < T_C + 40$ K, both $h(T)$ and $\sigma(T)$ are well represented by linear functions of T:

$$\sigma = \sigma_1 (T_C - T)/T_C, \tag{8a}$$

$$h = h_1 + h_2 T \tag{8b}$$

while the hopping parameter $\delta(T)$ follows an Arrhenius behavior

$$\delta = \delta_0 \exp(-E_0/T) \ . \tag{8c}$$

[$\delta(T)$ could equally well be fit with a Vogel-Fulcher form as suggested by DMN, but the precision of the $\delta(T)$ values was not high enough to warrant introducing a third parameter in Eq. (8c).]

Thus, with seven temperature-independent adjustable parameters (λ, σ_1, T_C, h_1, h_2, δ_0, E_0), the full set of susceptibility spectra spanning 80 K in T and over four decades in ω were fit with good precision. For the simplified analysis in which h is assumed constant and $\delta = 0$, the number of fitting parameters is reduced from 7 to 4. The parameter count of at least 12 and at least 8 suggested by ZKT thus appears to be seriously inflated. We add that Eqs. (8a,b) are not empirical guesses, but the result of a microscopic theory. For some simple examples such as hard spheres and binary mixtures, the five quantities λ, σ, T_C, h_1, and h_2 have been evaluated in the MCT literature from first principles.

In their Comment, ZKT propose an "alternative model" to explain our depolarized-light-scattering data. In essence, they postulate the existence of two independent processes: a strongly temperature-dependent α-relaxation process with a high-frequency ω^{-b} (von Schweidler) wing, and a second temperature-independent process which crosses over from $\chi''(\omega) \propto \omega^a$ for $\omega > \tau_\beta^{-1}$ to $\chi''(\omega) \propto \omega$ for $\omega < \tau_\beta^{-1}$. ZKT assert that this second (fast) process is "likely to be associated with dipole–induced-dipole (DID) interactions."

The *ad hoc* model of ZKT thus assumes the MCT result (1). It can be made to reproduce some idealized MCT predictions for $T > T_C$ by choosing τ_α and τ_β appropriately. But from Fig. 9 in Ref. [4] one sees that it cannot account for the data for $\omega < \omega_{\min}$ at $T = T_C + 5$ K or $T = T_C + 15$ K. Furthermore, for $T < T_C$, ZKT predict a temperature-independent knee which is not consistent with our data. ZKT suggest that their alternative model can describe the spectra, at least qualitatively, over the entire temperature range, but they *give no evidence* to support this assertion.

Another problem with this model is its prediction for the temperature-dependent intensity of the fast ω^a component. We find that the intensity in this frequency region increases rapidly as $T \to T_C$ from below. This effect was first observed in a neutron-scattering experiment [18] where the rapid increase of the *inelastic* scattering intensity as T increases above T_g coincides with a *decrease* of the elastic scattering intensity (i.e., the α process). This exchange of intensities, also seen in neutron-scattering studies of other materials, is a natural consequence of the T dependence of the plateau level predicted by the MCT, to be discussed below.

Looking at our susceptibility spectra in Refs. [2–4] one sees that the level of $\chi''(\omega)$ at frequencies above the minimum increases too rapidly with increasing T to be explained by simply adding the T-dependent α component to a temperature-independent ω^a contribution. In order to fit the data, one would need to also postulate an *ad hoc* temperature dependence for the fast ω^a component, for both light scattering and neutron scattering.

A particularly serious objection to the ZKT two-process alternative model concerns its obvious inability to explain neutron-scattering data on supercooled liquids. In the inelastic neutron-scattering spectrum $S_q(\omega)$, the frequency range of the intermediate β region of the susceptibility minimum corresponds to a two-power-law spectral region consisting of a low-frequency von Schweidler component with $S_q(\omega) \propto \omega^{-(1+b)}$ crossing over to a high-frequency critical component with $S_q(\omega) \propto \omega^{-(1-a)}$. The 1988 neutron scattering study of CKN by Knaak *et al.* [13] revealed this critical $\omega^{-(1-a)}$ component, establishing the existence of a two-step decay: the critical decay $f_c + A/t^a$ to the plateau f_c as the first step, and the α decay from the plateau to zero as the second. This two-step decay, which has also been observed in neutron-scattering studies of several other glass-forming materials, is generally regarded as consituting the most compelling evidence in favor of MCT. The frequency of the temperature-dependent susceptibility minimum for CKN reported by Knaak *et al.* (Fig. 4 of Ref. [13]) also agrees closely with our values (Fig. 8 of Ref. [2]).

Susceptibility minima have also been observed in other neutron-scattering experiments. In recent studies of glycerol [14] and orthoterphenyl [15], the frequency and temperature dependence of the $\chi''(\omega)$ minimum determined from neutron scattering was found to be in agreement with the $\chi''(\omega)$ minimum determined from light scattering. It is therefore highly unlikely that the dynamical processes underlying the light-scattering and neutron-scattering spectra in the frequency range around the $\chi''(\omega)$ minima are different. Since DID scattering does not apply to neutrons, the observation of the critical decay component and susceptibility minimum in both neutron scattering and light scattering experiments appears to provide a definitive test of the ZKT alternative model.

The principal target of the ZKT Comment is the cusp in τ_β, but they mistakenly identify τ_β as a "relaxation time." In order to clarify the significance of τ_β, we briefly summarize the relevant idealized MCT predictions. (For a complete description of these and other aspects of MCT, see [19].) MCT begins with a closed set of equations of motion for $\Phi_q(t)$, the normalized autocorrelation functions of the density fluctuation modes $\rho_q(t)$. The short-time (microscopic) behavior of $\Phi_q(t)$ is assumed to be that of a harmonic oscillator, but the subsequent time evolution is deduced entirely from self-consistent solutions of the equations. In contrast to the approach of ZKT, no power-law behavior is assumed.

Solutions to the MCT equations, even in the most simplified form, reveal that as the strength of the nonlinear interactions increases with increasing density (or decreasing temperature), $\Phi_q(t)$ decays more and more slowly until, at the crossover temperature T_C, a mathematical singularity (the GTS) occurs. At T_C, $f_q(T)$, the $t \to \infty$ limit of $\phi_q(t)$ suddenly increases from zero to f_q^c and then continues to increase with decreasing temperature as

$$f_q(T) = f_q^c + h_q\sqrt{\sigma} \qquad (T < T_C) . \tag{9}$$

Asymptotic expansions in the vicinity of the singularity led to several general predictions for $\Phi_q(t)$ in the intermediate time region between the short microscopic time and long α-relaxation time. This intermediate (β relaxation) region is centered at a time t_σ defined by

$$t_\sigma = t_0/|\sigma|^{1/2a}. \tag{10}$$

where t_0 is a microscopic time scale. In this intermediate time region, for temperatures above but close to T_C, $\phi_q(t)$ is given by

$$\phi_q(t) = f_q^c + h_q|\sigma|^{1/2} g_-(t/t_\sigma), \tag{11}$$

where

$$g_-(t/t_\sigma) = (t_\sigma/t)^a \qquad (t \ll t_\sigma). \tag{12}$$

$$g_-(t/t_\sigma) = -B(t/t_\sigma)^b \qquad (t \gg t_\sigma) . \tag{13}$$

Equations (11)–(13) predict the two-power-law decay of $\phi_q(t)$ subsequently observed in neutron-scattering experiments and the corresponding minimum in $\chi''(\omega) = \omega \int \cos(\omega t)\phi(t)dt$ for $T > T_C$, scaling behavior of $\phi_q(t)$ and $\chi''(\omega)$, and, below T_C, the temperature-dependent nonergodicity parameter $f_q(T)$ of Eq. (9). It is these predictions that nearly all experiments have attempted to test.

By combining Eqs. (10), (11), and (13) for $t \gg t_\sigma$, one finds

$$\phi_q(t) = f_q^c - Bh_q\left(\frac{t}{t_\alpha}\right)^b \qquad (t \gg t_\sigma), \tag{14}$$

with

$$t_\alpha = t_0|\sigma|^{-(\frac{1}{2a}+\frac{1}{2b})} . \tag{15}$$

Thus the von Schweidler decay, along with the rest of the α-relaxation process (usually approximated as a stretched exponential) to which it must join smoothly, moves to longer times with decreasing temperature following Eq. (15).

Similarly, by combining Eqs. (10)–(12) for $t \ll t_\sigma$, one finds

$$\phi_q(t) = f_q^c + h_q(t_0/t)^a \qquad (t \ll t_\sigma) \tag{16}$$

so that the form of the fast (critical decay) process is *essentially temperature independent.* [Equation (16) also holds for $T < T_C$.] Temperature dependence is introduced only through that of $h(T)$. Note that this remarkable set of predictions follows self-consistently from the MCT analysis. Every feature is a consequence of the time evolution of $\Phi_q(t)$. No "hidden processes" are invoked, and no specific spectral features are assumed. These results for $T > T_C$, which are obtained naturally from the MCT equations, are equivalent to the equations *postulated* by ZKT; that is why their alternate model can be equivalent to the idealized MCT for $T > T_C$.

In Fig. 1 we have plotted (schematically) three $\phi_q(t)$ curves: (a) for $T \gg T_C$, (b) for $T \gtrsim T_C$, and (c) for

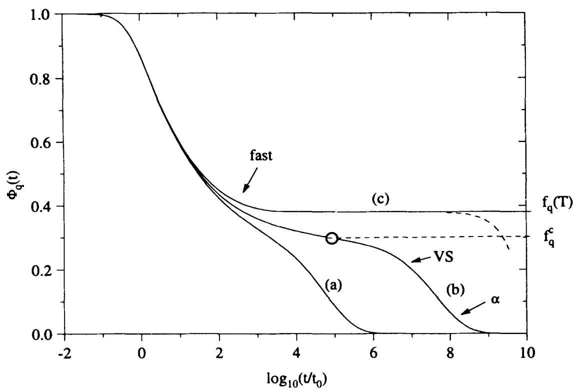

FIG. 1. Schematic idealized MCT correlation functions $\Phi_q(t)$ for a supercooled liquid at (a) $T \gg T_C$, (b) $T \gtrsim T_C$, and (c) $T < T_C$. The round point on (b) indicates the scaling time t_σ of Eq. (10), separating the fast (critical decay) t^{-a} process from the VS (von Schweidler) $-t^b$ decay which is the beginning of the primary α-relaxation process. The curving dashed line on curve (c) indicates the long-term ergodicity-restoring effects due to hopping processes. For $T < T_C$, the plateau moves upward with decreasing temperature while the form of the fast critical decay remains unchanged.

$T < T_C$. The solid point on (b) indicates t_σ, the inflection point which separates the critical decay $\sim t^{-a}$ from the von Schweidler decay $\sim -t^b$. As $T \to T_C^+$, t_σ moves towards $t = \infty$ following Eq. (10).

As T decreases below T_C, the flat plateau moves upwards with $\sqrt{\sigma}$ [Eq. (9)], and t_σ now represents a crossover between the fast t^{-a} critical decay and the t^0 plateau. The increasing height of the plateau with decreasing T has three principal consequences.

(1) The integrated area of the α peak, as measured by neutron scattering, increases for $T < T_C$ as $\sqrt{\sigma}$. Although the neglected hopping term eventually causes $\phi_q(t)$ to decay [as indicated by the dashed curving line on curve (c) in Fig. (1)], the finite experimental resolution available in practice means that the effective nonergodicity parameter $f_q(T)$ actually measured corresponds to the height of the plateau at a relatively early time. The predicted square-root cusp in $f_q(T)$ has been observed in several neutron-scattering experiments (for a review see [19]).

(2) The inelastic scattering should weaken rapidly as T decreases below T_C since its integrated intensity is proportional to $1 - f_q(T)$. The observation in neutron-scattering experiments of the fast relaxation process with a strongly temperature-dependent intensity as predicted by MCT has provided some of the strongest support for MCT.

(3) As the plateau moves up, the crossover point from t^{-a} to t^0 *must move towards shorter times.* From Eqs. (9) and (16) one sees that this crossover is given by Eq. (10). This is why the knee, i.e., the frequency at which $\chi''(\omega)$ crosses over from $\chi'' \propto \omega$ to $\chi'' \propto \omega^a$, must increase with decreasing T for $T < T_C$. This is the significance of the cusp in τ_β, which is proportional to τ_σ.

ZKT describe the temperature dependence of τ_β^+ as "a relaxation frequency increasing with decreasing temperature." We emphasize that the increase in τ_σ (or τ_β^+) as $T \to T_C$ from below does *not* imply a change in the time dependence of the fast decay process which is essentially temperature independent, and it does *not* represent a slowing down as discussed in phase transition theories in connection with soft-mode behavior. Nor is it a slowing down of a relaxation time scale as occurs for the α-relaxation process. Rather, it represents a shift of the crossover between $\phi_q(t) \propto t^{-a}$ and $\phi_q(t) =$const (and a resulting decrease of the scaling frequency ω_σ) as the plateau level decreases. At $T = T_C$ the crossover would approach $t = \infty$ in the idealized MCT, but the cutoff effect of the δ terms will always round off the cusp in t_σ. Furthermore, it should be recognized that the $\omega^{-(1-a)}$ critical spectrum *has no characteristic frequency* since, as a fractal (generalized $1/f$) spectrum, it contains all frequency scales. In this sense the critical decay spectrum of MCT is an analogue of the spatial correlations in thermodynamic phase transitions which, at the critical point, fall off as r^{-s} and are therefore spatially self-similar and so have no characteristic length scale.

Finally, we turn to a fundamental question which underlies both of the Comments. The original (idealized) MCT contained a single control parameter σ (initially designated as ϵ) which passes through $\sigma = 0$ at $T = T_C$. Consequently, the singularity (GTS) is directly traversed, divergences are complete, and simple one-parameter scaling laws are exact, at least asymptotically. In the extended MCT, there are two control parameters, σ and δ, which enter a two-parameter scaling law. So far it has not been possible to change σ and δ independently; both change with T so that the system passes close to, but not through, the GTS (as shown quantitatively in Figs. 3 and 5 of [4]). Consequently, divergences are rounded, one-parameter scaling is only approximate, and crossovers are smoothed. In the extended MCT, $\phi_q(t)$ and $\chi''(\omega)$ change smoothly and continuously with temperature, although the form of $\chi''(\omega)$ is significantly different for $T > T_C$ and $T < T_C$ [4]. Since the singularity is physically inaccessible and the sudden changes at $T = T_C$ predicted by the idealized theory are all smoothed, why should we believe that the GTS exists? Why, that is, do we need MCT?

We would respond that the GTS, though not physically accessible, still controls the supercooled liquid dynamics producing the two-power-law decay, the observed temperature dependence of both the effective nonergodicity parameter and the intensity of the fast relaxation process, and the detailed form and temperature evolution of the susceptibility spectra. The counterintuitive appearance of a cusp in the temperature-dependent scaling time found in our data and also found in correlation spectroscopy experiments on colloidal glasses [20] is also a direct consequence of the existence of the GTS. The ability of a coherent theoretical model to predict this striking array of unexpected effects (which have subsequently all been observed) gives very strong evidence for the essential correctness of MCT. We note that ZKT *postulate* the existence of two power-law regions in $\chi''(\omega)$, ω^{-b} and ω^a, which are singular functions of frequency while rejecting the existence of an underlying singularity. This is mathematically inconsistent. In the MCT these singular spectra appear as a natural consequence of the GTS which occurs in the solutions of the regular equations of motion.

We would suggest that when experimental data on the dynamics of supercooled liquids do not agree perfectly with the predictions of the idealized MCT, this should *not* be presented as evidence for the failure of MCT. The idealized MCT is a useful and convenient starting point for data analysis, but it is known to be an incomplete approximation to the existing full theory. A complete data analysis should be based on the extended MCT results. Our work, reported in [4], was an attempt to show that this is possible, and that the extended MCT does provide a more satisfactory understanding than its $\delta = 0$ simplified version. Whether or not the extended MCT will successfully fit the full range of experimental data, particularly $\chi''(\omega)$ spectra for $T < T_C$ which are just becoming experimentally accessible, is the real challenge which should be addressed.

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