Experimental Observation of a Nearly Logarithmic Decay of the Orientational Correlation Function in Supercooled Liquids on the Picosecond-to-Nanosecond Time Scales

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Dynamics of five supercooled molecular liquids have been studied using optical heterodyne detected optical Kerr effect experiments. "Intermediate" time scale power law decays (~ 2 ps to 1–10 ns) with temperature independent exponents close to -1 have been observed in all five samples from high temperature to $\sim T_c$, the mode-coupling theory (MCT) critical temperature. The amplitude of the intermediate power law increases with temperature as $[(T - T_c)/T_c]^{1/2}$. The results cannot be explained by standard MCT, and one possible explanation within MCT would require the higher order singularity scenario, thought to be highly improbable, to be virtually universal.

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The relaxation behavior of supercooled liquids and the nature of the glass transition have been intensely investigated in recent years using a variety of experimental techniques [1], but the dynamics of molecules in supercooled liquids are still poorly understood. Here, the results of optical heterodyne detected optical Kerr effect (OHD-OKE) experiments on the supercooled liquids, benzophenone (BZP) and 2-biphenylmethanol (BPM), are presented, and the previously obtained OHD-OKE results on ortho-terphenyl (OTP) [2], Salol [3], and dibutylphthalate (DBP) [4] are reanalyzed. The OHD-OKE experiment measures the time derivative of the polarizability-polarizability correlation function (orientational correlation function) [5]. The experiments were conducted over a broad range of times ($<$ ps to tens of ns), and a wide range of temperatures, from high T to $\sim T_c$, the mode-coupling theory (MCT) critical temperature. On the shortest time scales, <100 fs to ~ 1 ps, intramolecular vibrations strongly affect the data with pronounced oscillatory features. For times longer than the intramolecular vibrational damping times [2,3], ~ 2 ps, all five supercooled liquids exhibit temperature independent power law decays, t^{-1+c}, from ~ 2 ps to 1–10 ns with exponents close to -1. Therefore, the intermediate time portion of the correlation function decays as log$t$ or close to it. The amplitude power law increases with temperature as $(T - T_c)^{1/2}$.

Previous experiments, conducted mainly in the frequency domain, have either not observed the equivalent of the intermediate time scale power law or have seen it only at low temperature, close to or below T_g [6–8]. In the frequency domain, the equivalent of the "intermediate power law" occurs at the minimum of the susceptibility. Most frequency domain data have been fit piecewise with MCT using the first order terms to describe the fast β relaxation (high frequency) and the von Schweidler relaxation (low frequency). Errors in fitting are difficult to detect around the minimum. However, at low temperatures, it was found necessary to add a "near constant loss" term to the MCT fitting functions to descibe the region of the minimum of the susceptibility curve [6,8]. The near constant loss term in the frequency domain becomes a power law decay in the time domain optical Kerr experiments. Prior time domain experiments reported the intermediate power law [2–4], but it was interpreted as the failure of ideal MCT only as the temperature passed through T_c. None of the previous results suggested the existence of temperature independent power laws at elevated temperatures as a universal feature of supercooled liquid dynamics and as a clear failing of the standard MCT model to describe the intermediate time dynamics of supercooled liquids.

In Fig. 1, log plots of a few of the OHD-OKE data sets for BZP and BPM are shown at various temperatures from T_c to well above T_c. For display purposes, the curves are normalized at 300 fs. This normalization is not used in the data analysis. Fits to the data, discussed below, are also shown. The analysis focuses on $t \geq 2$ ps to avoid interference from stimulated Raman excitation of internal molecular vibrations [4]. The intermediate power law begins at $\sim$1–2 ps; it has an exponent close to -1 (-0.9 in BPM and -0.87 in BZP) and lasts for 3 to 4 decades at $T \cong T_c$ (see below). The dashed lines in the figure are aids to the eye. Following the intermediate power law is a crossover region immediately preceding the final exponential decay. The crossover region, known as the von Schweidler power law, is the onset of complete structural relaxation, the α relaxation [2,3,9,10]. As the temperature is increased above T_c, both the intermediate and von Schweidler power law regions shorten.

We fit the experimental curves for $t > \sim 2$ ps with a fitting function, $F(t)$,

$$F(t) = [pt^{-1+c} + dt^{b-1}]\exp(-t/\tau_\alpha). \qquad (1)$$

The first term with $c \ll 1$ corresponds to the intermediate power law; the second term is akin to the von Schweidler power law; the exponential function describes the final

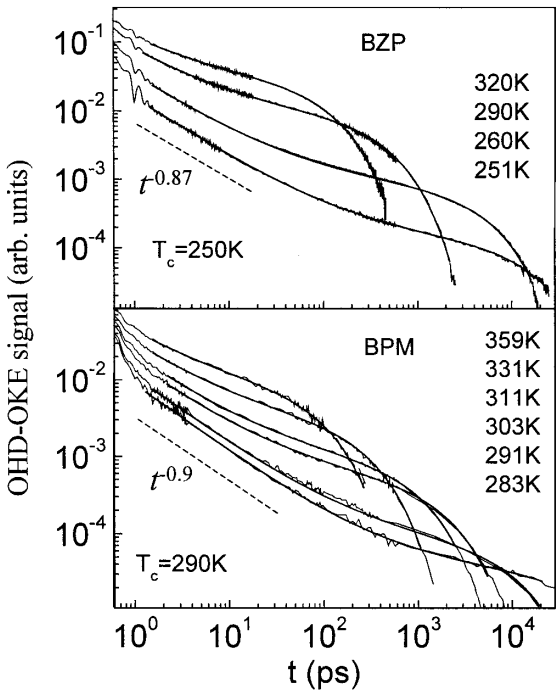

FIG. 1. A log plot of OHD-OKE data for BZP and BPM for a few of the temperatures investigated. Also shown are fits to the data using Eq. (1). The dashed lines are aids to the eye indicating the presence of the intermediate power law.

α-relaxation decay. The product of the von Schweidler power law and the exponential have been previously shown to describe the longer time portion of the OHD-OKE data for several supercooled liquids extremely well [2–4]. Frequently, the long time portion of the correlation function is described as a stretched exponential. Using the time derivative of a stretched exponential to describe the OHD-OKE experiment adds another power law and more parameters in the fit. We found that employing the time derivative of a stretched exponential did not improve the fit.

The two power law exponents and the exponential time constant are determined by globally fitting all temperature curves at $t > \sim 2$ ps. τ_α is essentially independent of the other parameters. When each curve is fit individually, the results are basically the same. In particular, the intermediate power law exponents were found to be temperature independent. The global fit is useful at the higher temperatures at which the von Schweidler power law spans only a short range, and its exponent is difficult to determine. In Fig. 1 the fits for some selected temperatures are shown. Equation (1) does a very good job in fitting the decay curves for BZP and BPM at various temperatures over a broad time range. There is no increasing systematic deviation between the data and the fits as T_c is approached, and for some samples, passed below. This is in contrast to fits using standard MCT [2–4]. Therefore, there is no change in the form of the data at T_c. The data for OTP [2], Salol [3], and DBP [4] (not shown here) are fit equally well. The power law exponents and their amplitudes are very robust in these fits.

Using the MCT scaling relations for the temperature dependence of τ_α and the amplitude of the von Schweidler term d [10], rectification diagrams were constructed for each sample [2,3]. The two scaling laws were confirmed, and the rectification diagrams for both scaling laws yield the same critical temperatures T_c (see Table I). Thus, the long time scale relaxation is in agreement with the predictions of standard MCT.

Figure 2 displays log plots of the intermediate power law portions of the data for all five liquids with the contributions from the von Schweidler term and the α relaxation removed. The data are straight lines over 3 to 4 decades of time. The power law portions of the data for BPM at various temperatures are shown in Fig. 3. Data for the other samples are similar. For each liquid at all temperatures, temperature independent intermediate time scale power law decays are observed. The power law exponents are give in Table I.

MCT describes kinetic phenomena in terms of a nonlinear feedback mechanism. Different types of singularities in the equations can be classified as A_l, $l = 2, 3, \ldots$. Near the simplest singularity, A_2, MCT predicts a two-step relaxation process consisting of a fast β process followed by a slow α process. The intermediate power law region is not consistent with the standard presentations of MCT, although the long time portions of the experimental observations are well described by the MCT two-step scenario above T_c [10].

The relations obtained for the A_2 singularity provide the standard MCT results that are frequently compared to data [10]. The MCT equations are solved numerically, but accurate series approximations have been obtained [11]. The results are, for times $t_0 < t \leq t_\sigma$,

$$\phi_q(t) = f_q^c + h_q|\sigma|^{1/2}[(t/t_\sigma)^{-a} - A_1(t/t_\sigma)^a + A_2(t/t_\sigma)^{3a} - A_3(t/t_\sigma)^{5a} + \cdots], \quad (2)$$

and, for $t_\sigma < t \leq \tau_\alpha$,

$$\phi_q(t) = f_q^c + h_q|\sigma|^{1/2}[-B(t/t_\sigma)^b + (B_1/B)(t/t_\sigma)^{-b} + \cdots]. \quad (3)$$

TABLE I. The values of the exponents and critical temperatures.

	b	c	T_c
BZP	0.85 ± 0.03	0.13 ± 0.03	250 ± 4
BPM	0.8 ± 0.03	0.1 ± 0.03	290 ± 4
Salol	0.84 ± 0.03	0 ± 0.03	260 ± 4
OTP	0.73 ± 0.03	0.15 ± 0.03	290 ± 4
DBP	0.85 ± 0.03	0.21 ± 0.03	234 ± 4

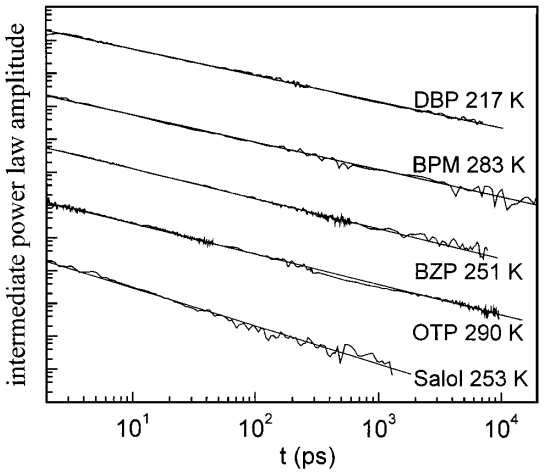

FIG. 2. The intermediate power law decays (displaced along the vertical axis for clarity) for DBP, BPM, BZP, OTP, and Salol supercooled liquids at or near T_c. The power laws extend for 3–4 decades.

$t_\sigma = t_0|\sigma|^{-1/2a}$ is a rescaling time. The microscopic time t_0 is a constant, and the exponent $a < 0.5$. The separation parameter $\sigma = (T - T_c)/T_c$. The relation between the exponents a and b is given by $\lambda = \Gamma^2(1-a)/\Gamma(1-2a) = \Gamma^2(1+b)/\Gamma(1+2b)$. At long time, Eq. (3) becomes the von Schweidler power law with exponent b.

Equations (2) and (3) combined do not decay as log$t$, and the time derivative of Eqs. (2) and (3) does not describe an extended intermediate time scale power law [2,4]. Therefore, the standard MCT description of dynamics obtained for the A_2 singularity cannot explain an OHD-OKE experimental observation of an intermediate power law.

Recently, it was shown that in some special systems another mechanism could contribute significantly to relaxation dynamics. The "end point" scenario, which corresponds to higher order singularities, e.g., A_3, leads to an *approximately* logarithmic time dependence of the correlation function. Systems with interparticle potentials that can be represented by a hard core repulsive and a square well short range attractive parts are expected to exhibit the logarithmic time dependence. Both analytical estimates and computer simulations confirm that this type of system exhibits an approximately log$t$ dependence of the density correlation function [12–15]. Such behavior was observed experimentally by photon-correlation spectroscopy of colloids [16]. In the frequency domain, the contribution to the susceptibility has a $1/f$ noiselike spectrum. Near the A_3 singularity, the leading order contribution is [17,18]

$$\phi_q = f_q^c - B_1 h_q \log(t), \qquad B_1 = \sqrt{6\sigma}. \tag{4}$$

It has also been shown that this logarithmic decay can cross over to the von Schweidler power law decay at longer times [17]. The logarithmic term, if any, gives a contribution to the OHD-OKE signal

$$S_{\log} \propto \frac{d\phi_q}{dt} = -B_1 h_q t^{-1}. \tag{5}$$

The exponent parameter c that describes the deviation of the intermediate power law term from the pure logarithmic behavior of the experimental correlation function $f(t)$ is small for all five liquids investigated (see Table I). For $c \neq 0$, the respective term in $f(t)$ is not exactly log$t$, but a power law with a small exponent c, $f(t) \propto t^c$ is

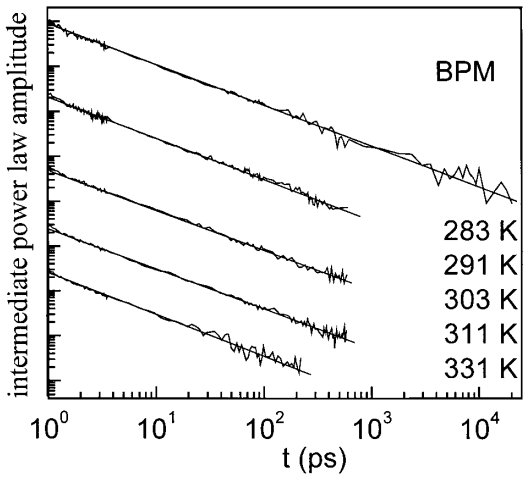

FIG. 3. Log plots of the intermediate power law portions of the BPM data (displaced along the verical axis for clarity) for the five temperatures demonstrating temperature independence of the power law exponent.

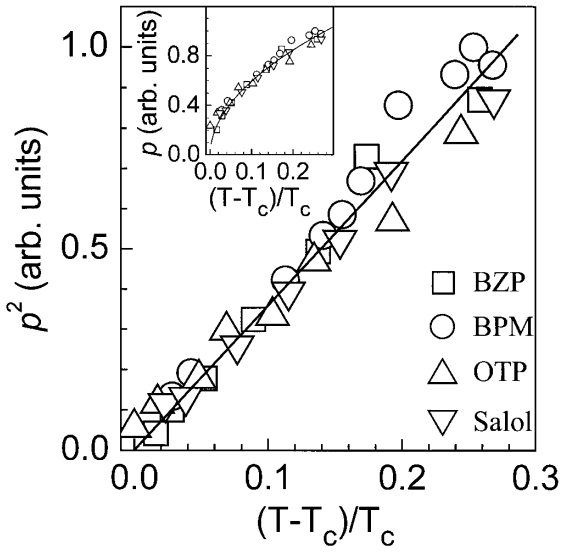

FIG. 4. The amplitudes p of the intermediate power laws of BPM, BZP, OTP, and Salol supercooled liquids plotted as p^2 vs $(T - T_c)/T_c$. The vertical scales are normalized so plots overlap. The points fall on a line. Inset: p plotted vs $(T - T_c)/T_c$. The curve through the data is a fit to $[(T - T_c)/T_c]^{1/2}$.

barely distinguishable from log$t$, particularly over a limited time range.

Because the MCT end point scheme that gives rise to the log$t$ decay of the correlation function is thought to apply only for special properties of the system, it would not be expected to contain the explanation for the intermediate power law decays of the data in all five liquids studied. However, the temperature dependence of the amplitude of the intermadiate power law is suggestive that general observation of the power law decay for molecular supercooled liquids may arise from the end point scenario.

The temperature dependence of the amplitude p of the intermediate power law term [Eq. (1)] is shown in Fig. 4 in terms of the reduced temperature $(T - T_c)/T_c$. According to Eqs. (3) and (4), p should scale as $[(T - T_c)/T_c]^{1/2}$. To obtain p at each temperature, taking into account changes in laser intensity over time, the data sets were normalized to the peak of the electronic polarization contribution to the signal, which is almost temperature independent ($< 7\%$ change over the temperature ranges of the experiments) and occurs only at $t = \sim 0$ [3].

Figure 4 shows p^2 as a function of $(T - T_c)/T_c$. The line through the data is a fit to the points. The inset shows the points plotted as p vs $(T - T_c)/T_c$. The solid curve is a fit with $p \propto [(T - T_c)/T_c]^{1/2}$. Figure 4 clearly demonstrates that the amplitude of the intermediate power law is a square root function of $(T - T_c)/T_c$ for all four liquids in accordance with Eq. (4). Therefore, the orientational correlation functions decay with time and temperature dependences that are consistent with the MCT end point case. The results can be viewed as providing some support for the possibility that the intermediate power law is related to a MCT high order singularity.

As currently understood, the MCT end point case [13,17,18] does not seem capable of explaining the apparent universality of a nearly log$t$ term in $f(t)$ for molecular liquids. The infrequency of the end point case comes about because the trajectory of the system in the parameter space of the mode-coupling functional normally intersects the boundary of the glass transition hypersurface (end point of the glass transition line in the schematic two parameter model [18]) with a probability close to zero. However, contrary to the MCT schematic models, the phase space of the mode-coupling parameters for molecular systems may be very large, nearly infinite dimensional, because the intermolecular potentials are complex. In such a space, it might be possible for the glass transition hypersurface to have a complex form with nearly chaotic boundaries that would make the approach to such boundaries common rather than rare. The MCT end point case needs to be investigated and generalized before it can be considered an explanation for the observations.

In this Letter we have (i) shown a heretofore unknown feature of the dynamics of supercooled liquids, i.e., an apparently universal temperature independent intermediate time scale nearly logarithmic decay of the orientational correlation function, (ii) pointed out that the form of MCT used normally cannot explain the observations, and (iii) that there is a version of MCT, thought not to apply to real systems, that has substantial agreement with the data. (iv) Our data call into question the utility of MCT unless substantial new MCT theory is developed that shows what is thought to be highly improbable is actually virtually universal. Gaining an understanding of the intermediate power law may be a key that will unlock a comprehensive description of supercooled liquids and the glass transition.

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