

# Dynamical signature of two “ideal glass transitions” in nematic liquid crystals

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A temperature scaling analysis using the same mode coupling theory (MCT) scaling relationships employed for supercooled liquids is applied to optical heterodyne detected optical Kerr effect data for four liquid crystals. The data cover a range of times from  $\sim 1$  ps to 100 ns and a range of temperatures from  $\sim 50$  K above the isotropic to nematic phase transition temperature  $T_{NI}$  down to  $\sim T_{NI}$ . The slowest exponential component of the data obeys the Landau–de Gennes (LdG) theory for the isotropic phase of liquid crystals. However, it is also found that the liquid crystal data obey MCT scaling relationships, but, instead of a single scaling temperature  $T_C$  as found for supercooled liquids, in the liquid crystals there are two scaling temperatures  $T_{CL}$  ( $L$  for low temperature) and  $T_{CH}$  ( $H$  for high temperature).  $T_{CH}$  is very close to  $T^*$ , which results from LdG scaling, just below the isotropic to nematic phase transition temperature,  $T_{NI}$ , but is 30–50 K higher than  $T_{CL}$ . The liquid crystal time dependent data have the identical functional form as supercooled liquid data, that is, a fast power law decay with temperature independent exponent, followed by a slower power law decay with temperature independent exponent, and on the longest time scales, an exponential decay with highly temperature dependent decay constant. For each liquid crystal, the amplitudes of the two power laws scale with expressions that involve  $T_{CL}$ , but the exponential decay time constant (long time dynamics) scales with an expression that involves  $T_{CH}$ . The existence of two scaling temperatures can be interpreted as a signature of two “glass transitions” in liquid crystals. In ideal MCT developed for spheres,  $T_C$  is the “ideal glass transition temperature,” although it is found experimentally to be  $\sim 20\%$ – $30\%$  above the experimental glass transition temperature,  $T_g$ . The transition in nematic liquid crystals at  $T_{CL}$  corresponds to the conventional ideal MCT glass transition, while the transition at  $T_{CH}$  can occur for nonspherical molecules, and may correspond to the freezing in of local nematic order. © 2003 American Institute of Physics.  
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## I. INTRODUCTION

The dynamics of liquid crystals in their isotropic phase are complex, occurring over a wide range of time scales.<sup>1–6</sup> Liquid crystals have a well-defined mesoscopic scale physical picture of the nematogens in the isotropic phase,<sup>3,4,7,8</sup> and this physical picture provides insights for the still evolving theoretical description of liquid crystal dynamics.<sup>4</sup> Above but near the nematic–isotropic (N–I) phase transition temperature,  $T_{NI}$ , ( $T_{NI} < T < T_{NI} + \sim 50$  K), orientational relaxation dynamics are strongly influenced by local structures (pseudonematic domains) that exist in the isotropic phase.<sup>7,8</sup> A great deal of experimental work has been done using both time and frequency domain methods to examine the relatively long time scale orientational relaxation that is dominated by the randomization of the pseudonematic domains.<sup>1,3,9–15</sup> Near the N–I phase transition, the isotropic phase is nematically ordered on a distance scale defined by a correlation length,  $\xi$ .<sup>7,8</sup> As the N–I phase transition is approached from above,  $\xi$  grows, becoming infinite in the nematic phase. On time scales of many nanoseconds to hundreds of nanosec-

onds, depending on the temperature, the local order randomizes, giving rise to exponential decays in time domain optical Kerr effect experiments.<sup>3,5,9</sup>

In contrast to liquid crystals, there is no mesoscopic distance scale physical picture for supercooled liquids that spans a wide range of temperatures. Supercooled liquids and the approach to the glass transition have attracted a tremendous amount of experimental and theoretical interest<sup>16,17</sup> because of the complexity of the dynamics of these nonthermodynamic equilibrium systems and the technological importance of the glass transition and glasses. Although there have been a great number of experimental studies of supercooled liquids,<sup>17–37</sup> the relationship between the mesoscopic scale structure and the dynamics is unclear. Very close to the glass transition temperature,  $T_g$ , there have been a number of experiments that suggest supercooled liquids are structurally heterogeneous.<sup>38,39</sup> Simulations on spheres<sup>40,41</sup> and somewhat more complex shapes<sup>42–44</sup> provide insights, but they cannot address whether supercooled liquid inhomogeneity that is observed very close to  $T_g$  persists at much higher temperatures and whether inhomogeneity is important in determining dynamics well above  $T_g$ . In the discussion of the dynamics of supercooled liquids, particularly at temperatures significantly above  $T_g$ , ideal mode-coupling theory<sup>45–48</sup>

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(MCT) has played a significant role because it makes testable predictions of temperature dependent dynamics.<sup>35,49</sup>

Recently, a great deal of effort has been directed toward understanding the complex relaxation behavior in molecular liquids, including both supercooled liquids and liquid crystals, in a unified manner.<sup>44,50–55</sup> The research involves the interplay between orientational degrees of freedom and translational degrees of freedom. This effort dates back to Onsager's pioneering work on hard rods.<sup>56</sup> Tanaka proposed that a competition between multiple order parameters may lead to the glass transition.<sup>50</sup> Schilling and co-workers put forward a "molecular mode coupling theory,"<sup>44,52</sup> an extension of MCT that includes the orientational degrees of freedom. Rzoska *et al.* performed linear and nonlinear dielectric relaxation measurements that suggested a glass transition for the liquid crystal 5-CB well below the isotropic to nematic phase transition.<sup>51</sup>

A very recent optical heterodyne detected optical Kerr effect (OHD-OKE) study of the orientational dynamics of isotropic phase liquid crystals near the isotropic to nematic transition demonstrated the liquid crystal dynamics are essentially identical to those of the supercooled liquids.<sup>55</sup> On time scales sufficiently long such that the observations are not dominated by intramolecular vibrational degrees of freedom ( $> \sim 1$  ps), both types of liquids decay with a temperature independent power law, the "intermediate power law," followed by a crossover region that can be described as a second power law, the von Schweidler power law.<sup>6,35,49,55</sup> The final, complete structural relaxation is a highly temperature dependent exponential decay.<sup>6,35,49,55</sup>

The data for all nine liquids studied, five supercooled liquids and four liquid crystals, are fit very well with

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

The first term with  $z \leq 1$  corresponds to the intermediate power law. (The name intermediate power law is used to distinguish it from the MCT fast  $\beta$  power law, and the von Schweidler power law.<sup>32,45,57–60</sup> The intermediate power law has been found to be a general feature of fragile supercooled liquids, in contrast to the predictions of standard MCT.<sup>35,49</sup>) The second term is the crossover power law that reflects the onset of complete structural relaxation. In supercooled liquids, it is called the von Schweidler power law. We will use the same name for liquid crystals. Values of  $b$  were found to vary between 0.73 and 0.98 for all the supercooled liquid and the liquid crystal samples.<sup>55</sup> The exponential term is associated with the final complete structural relaxation. The exponential decay is called the primary relaxation, the structural relaxation, or the  $\alpha$  relaxation in supercooled liquids. In liquid crystals, the long time scale exponential decay is often referred to as the Landau–de Gennes (LdG) decay. We will use the name  $\alpha$  relaxation to describe the long time exponential decay in both types of liquids. Figure 3 in Ref. 55 displays data and fits to Eq. (1) for supercooled liquids and liquid crystals, demonstrating that Eq. (1) fits data from both types of liquids very well. It was conjectured that the similarities between the liquid crystal data and the supercooled liquid data are produced by the same underlying physical

features, that is, like liquid crystals, supercooled liquid dynamics are a result of structural domains even at relatively high temperatures.<sup>55</sup>

In this paper, we will address another aspect of liquid crystals that shows a striking resemblance to the temperature dependent properties of supercooled liquids analyzed in terms of MCT. MCT predicts certain temperature scaling relationships.<sup>45,57–59</sup> The amplitude of the von Schweidler power law [see Eq. (1)] scales as

$$d \propto (T - T_C)^\delta, \\ \delta = (a + b)/2a. \quad (2)$$

$b$  is the von Schweidler power law exponent and  $a$  is related to  $b$  by

$$\Gamma^2(1-a)/\Gamma(1-2a) = \Gamma^2(1+b)/\Gamma(1+2b), \quad (3)$$

where  $\Gamma$  is the gamma function. The exponential decay time constant  $\tau_\alpha$  increases with decreasing temperature as

$$\tau_\alpha \propto (T - T_C)^{-\gamma}, \\ \gamma = (a + b)/2ab. \quad (4)$$

Standard MCT does not predict the existence of the intermediate power law.<sup>35,49</sup> MCT describes kinetic phenomena in terms of a nonlinear feedback mechanism. Different types of singularities in the equations can be classified as  $A_l$ ,  $l = 2, 3, \dots$ . The MCT results for supercooled liquids are generally taken to be the solutions to the kinetic equations near the simplest singularity,  $A_2$ . However, 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.<sup>61–64</sup> Because the OHD-OKE experiment measures the time derivative of the polarizability–polarizability correlation function (orientational correlation function), the approximately logarithmic decay of the correlation function will give rise to a power law approximately  $t^{-1}$ , as observed.<sup>35,49</sup> The end point scenario is believed to only apply in very special circumstances that would not occur in simple supercooled liquids. This is in contrast to recent experiments that indicate the near logarithmic decay of the correlation function may be a universal feature of supercooled liquids.<sup>35,49</sup> The higher order singularity solutions to the MCT equations give rise to a scaling relationship for the amplitude of the intermediate power law [see Eq. (1)], that is,

$$p \propto \sqrt{T - T_C}. \quad (5)$$

Equation (5) has been found to hold for supercooled liquids.<sup>35,49</sup>

In the scaling relations given in Eqs. (2), (4), and (5), the MCT critical temperature  $T_C$  is the unique scaling temperature. In this paper we show that the MCT scaling relationships given above are also operative for the four liquid crystals that have been studied over the full range of time scales.<sup>4–6,55</sup> However, unlike supercooled liquids, two scaling temperatures,  $T_{CL}$  ( $L$  for low temperature) and  $T_{CH}$  ( $H$  for high temperature), are found. The amplitude of the intermediate power law  $p$  and the amplitude of the longer time scale von Schweidler power law  $d$  increase with temperature

as  $p \propto \sqrt{T - T_{CL}}$  and  $d \propto (T - T_{CL})^\delta$ . In contrast, the exponential decay time constant  $\tau_\alpha$  increases with decreasing temperature as:  $\tau_\alpha \propto (T - T_{CH})^{-\gamma}$ .  $T_{CL}$  is 40–50 K lower than  $T_{CH}$ . Both  $T_{CL}$  and  $T_{CH}$  are below the isotropic to nematic phase transition temperature,  $T_{NI}$ .  $T_{CH}$  is a few degrees below  $T_{NI}$  and very close to  $T^*$ , the nominal second-order phase transition temperature.<sup>8</sup>

In ideal MCT,  $T_C$  is the ideal glass transition temperature, although it is found experimentally to be  $\sim 20\%$  above the true glass transition temperature,  $T_g$ . The existence of two scaling temperatures,  $T_{CL}$  and  $T_{CH}$ , suggests an interpretation in which there are two ideal glass transitions in liquid crystals. The low temperature one is the equivalent of the MCT  $T_C$  for supercooled liquids, the ideal glass transition. The higher temperature one is distinct because liquid crystals undergo a real phase transition at  $T_{NI}$ , in contrast to supercooled liquids. The reason for the two transitions will be discussed in terms of a qualitative physical picture.

## II. EXPERIMENTAL PROCEDURES

The results that will be discussed in the following have been presented previously.<sup>55</sup> The four liquid crystals studied are: 4'-(pentyloxy)-4-biphenylcarbonitrile (5-OCB),<sup>5</sup> 4'-pentyl-4-biphenylcarbonitrile (5-CB)<sup>5</sup> and 1-isothiocyanato-(4-propylcyclohexyl)benzene (3-CHBT),<sup>4,5</sup> and 4'-Octyl-4-biphenylcarbonitrile<sup>6</sup>(8-CB).

The experiments were conducted using the optical heterodyne detected optical Kerr effect (OHD-OKE) experiment. The OHD-OKE experiment, a nonresonant pump-probe technique, measures the time derivative of the polarizability-polarizability correlation function (orientational correlation function).<sup>65,66</sup> The pump pulse induces an optical anisotropy. The induced optical anisotropy decays because of orientational relaxation. The decay is measured with a time delayed probe pulse. The Fourier transform of the OHD-OKE signal is directly related to data obtained from depolarized light scattering.<sup>67</sup> Further details can be found in the previous publications of the data.<sup>4–6,55</sup>

To obtain the temperature scaling relations of the amplitudes of the two power laws, it is necessary to normalize the data to correct for the effects of laser intensity drift and sample density change when the temperature is changed. At  $t=0$ , the OHD-OKE signal is overwhelmingly dominated by the instantaneous electronic response of samples. Since both the density changes caused by temperature variation and any laser intensity drift have the same effect on the nuclear part and the electronic part of OHD-OKE signals, the OHD-OKE orientational relaxation data were normalized to the instantaneous electronic response at  $t=0$ . The change of the  $t=0$  electronic peak arising from the temperature change was measured and found to be small, 5%–10% depending on the sample. Therefore, any error in the correction is a small error in a relatively small correction.

## III. RESULTS AND ANALYSIS

It has been shown previously that Eq. (1) fits the liquid crystal OHD-OKE data very well.<sup>55</sup> The temperature independent parameters obtained for the four liquid crystals are

TABLE I. Temperature independent parameters obtained from fits to Eq. (1) and from the scaling relations, Eqs. (2)–(4).

Liquid crystal	$z$	$b$	$a$	$\delta$	$\gamma$
3-CHBT	$0.78 \pm 0.02$	0.96	0.389	1.734	1.806
5-CB	$0.65 \pm 0.02$	0.95	0.388	1.724	1.815
5-OCB	$0.63 \pm 0.02$	0.95	0.388	1.724	1.815
8-CB	$0.54 \pm 0.02$	0.98	0.392	1.75	1.787

given in Table I.  $z$  is the intermediate power law exponent, which describes the power law from  $\sim 1$  ps to the crossover region.  $b$  is the von Schweidler power law exponent that describes the crossover region.  $a$  is the quantity derived from  $b$  using Eq. (3) that appears with  $b$  in the scaling relations, Eqs. (2) and (4).  $\delta$  is the scaling exponent for the amplitude of the von Schweidler power law [Eq. (2)], and  $\gamma$  is the scaling exponent for the  $\alpha$  relaxation time constant [Eq. (4)].

Some features of the parameters will be described briefly here. The power law exponent of the intermediate power law  $t^{-z}$  is temperature independent.  $z$  decreases as the aspect ratio of the liquid crystal increases.<sup>65,55</sup> A linear extrapolation shows that the value of  $z$  would be  $\sim 0.85$  when the aspect ratio is 2.5, the value at which theory indicates that a nematic phase will no longer exist.<sup>68</sup>

The liquid crystal von Schweidler power law exponents  $b$  have larger values than those of the supercooled liquids. For supercooled liquids, the von Schweidler exponent  $b$  is in the range 0.73–0.85 for the five supercooled liquids studied.<sup>35,49</sup> The liquid crystal  $b$  is in the narrow range 0.95–0.98. If  $b=1$ , the von Schweidler power law would vanish [see Eq. (1)]. However, it was found that the liquid crystal data could not be fit well without a crossover regime reflected by the von Schweidler power law.

The long time exponential decays obey Landau–de Gennes mean field theory well.<sup>5,6,8</sup> The exponential decay time constant  $\tau_{LdG}(T)$  diverges at the transition temperature  $T^*$  as<sup>3,5,6,8,9,69</sup>

$$\tau_{LdG} \propto \frac{V_{\text{eff}} \eta(T)}{T - T^*}, \quad (6)$$

where  $\eta(T)$  is the viscosity,  $V_{\text{eff}}$  is the nematogen's effective volume.  $T^*$  is generally about one degree below  $T_{NI}$ . Figure 1 plots the temperature dependent exponential decay time  $\tau_\alpha$  ( $\tau_{LdG}$ ) versus temperature for one of the liquid crystals, 8-CB. The extrapolated temperature  $T^*$  is 313 K, which is very close to  $T_{NI}=313.5$  K. The other liquid crystals display similar behavior.

As discussed earlier, for supercooled liquids the temperature-scaling relations [Eqs. (2)–(5)] have been found within the framework of MCT to apply to five supercooled liquids.<sup>35,49</sup> Figures 2(a)–2(d) show “rectification” plots for the parameter  $d$ , that is,  $d^{1/\delta}$  vs  $T$  for all the four liquid crystals. Data are normalized for purpose of comparison. The parameter  $\delta$  is obtained using the fitting values of the von Schweidler exponent  $b$  and the parameter  $a$  found from Eq. (3). If the data obey the scaling relation, the points should fall on a line, and the intercept is  $T_{CL}$ .  $T_{CL}$  would be called  $T_C$  if there is only one scaling temperature as found in su-

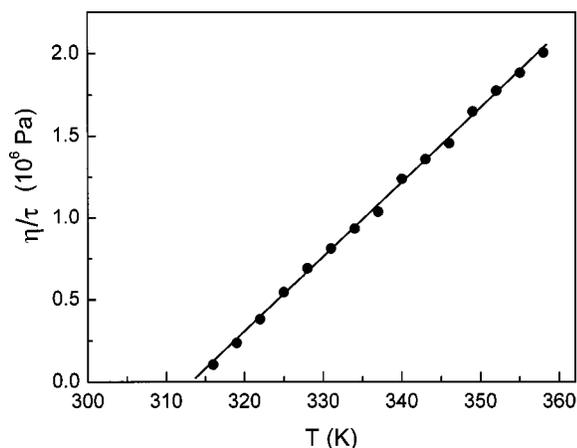


FIG. 1. The temperature dependent exponential relaxation times,  $\tau_\alpha$ , for the liquid crystal 8-CB plotted as  $\eta/\tau_\alpha$  vs  $T$ . The solid line through the points is the Landau–de Gennes theoretical curve (Eq. 6), with  $T^*$  the extrapolated “clearing” temperature which is very close to  $T_{NI}=313.5$  K, in accord with LdG theory.

percooled liquids. The rectification plots for all the four liquid crystals exhibit linear temperature dependencies within experimental error. The extrapolated critical temperatures  $T_{CL}$  are given in Table II.  $T_{CL}$  is 40–50 K below  $T_{NI}$ . The rectification plots of  $\gamma$ , that is,  $\tau_\alpha^{-1/\gamma}$  vs  $T$ , for the liquid crystals are also shown in Figs. 2(a)–2(d). Again, within experimental error, the points for all four liquid crystals fall on a line, demonstrating that the scaling relation in Eq. (4) is obeyed. The extrapolated temperatures from Eq. (4),  $T_{CH}$  are given in Table II. The two temperature scaling relations give two critical temperatures separated by 40–50 K. The difference in the critical temperatures is distinct from what is observed for supercooled liquids. Figure 3 shows the same type of rectification diagrams for the von Schweidler power law decay amplitude  $d$  and the exponential decay time constant  $\tau$  for a supercooled liquid, 2-biphenylmethanol.<sup>35</sup> In this case, the two scaling relations give the same  $T_C$  within experimental error. This is also true for other supercooled liquids.<sup>32–35</sup> It is also interesting to note that the scaling relationship for  $\tau_\alpha$  [Eq. (4)] describes the temperature dependence of the exponential decay times well, perhaps as well as the LdG formula, Eq. (6).

Figure 4 presents the scaling relation [Eq. (5)] for the temperature dependence of the intermediate power law amplitude  $p$  as  $p^2$  vs  $T$ . The quality of the data is not as good as that of Figs. 2 and 3. Nonetheless, it is clear that the scaling relation is obeyed, possibly with the exception of the 8-CB data where the spread in the points is large. The lines were

TABLE II. Characteristic temperatures of the liquid crystals.

Liquid crystal	$T_{CH}$ (K)	$T^*$ (K)	$T_{NI}$ (K)	$T_{CL}$ (K)	$T_g$ (K)	$T_{CL}/T_g$
3-CHBT	308±2	312±2	314.7	250±2		
5-CB	306±2	308±2	308	268±2	210 <sup>a</sup>	1.3
5-OCB	340±2	344±2	344	292±2		
8-CB	312±2	313±2	313.5	277±2		

<sup>a</sup>From ref. 73.

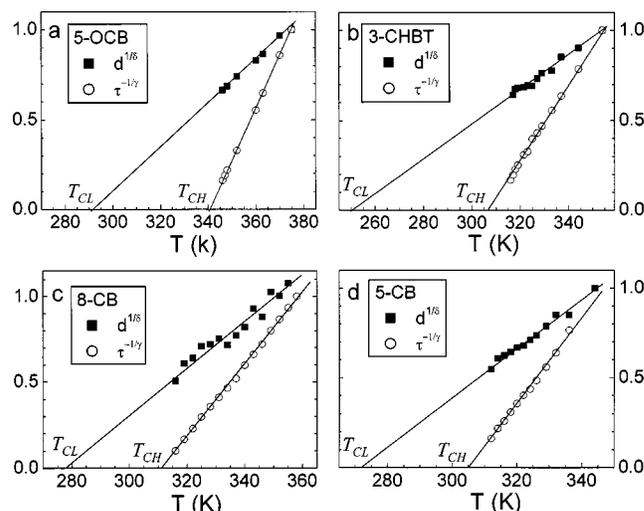


FIG. 2. The temperature dependence of the amplitude of the von Schweidler power law  $d$  (squares, plotted as  $d^{1/\delta}$ ) and the exponential relaxation time  $\tau_\alpha$  (circles, plotted as  $\tau_\alpha^{-1/\gamma}$ ) for four liquid crystals. (a) 5-OCB, (b) 3-CHBT, (c) 8-CB, (d) 5-CB. Solid lines are fits to Eqs. (2) and (4), demonstrating that the data obey the MCT scaling relations but yielding two critical temperatures,  $T_{CL}$  and  $T_{CH}$  obtained by extrapolation. The data sets’ amplitudes were adjusted so that they could be shown on the same plot. The change in amplitude does not affect the agreement with the scaling relations.

drawn using  $T_{CL}$  found from Fig. 2, not as an adjustable parameter. Supercooled liquids display the same scaling relations, but the data are better because it can be obtained over a wider range of temperatures.<sup>35,49,55</sup> The intermediate power law exponents  $z=0.54$ – $0.78$  in the liquid crystals are farther from 1 than those of the supercooled liquids. According to MCT, the logarithmic decay is a signature of higher order singularities in the MCT solutions.<sup>61–64</sup> The temperature scaling relation  $p \propto (T - T_C)^{1/2}$  occurs for a solution near a MCT higher order singularity, not from the standard MCT lowest order singularity solution.<sup>61–64</sup> However, the  $p \propto (T - T_C)^{1/2}$  relation has been observed for a number of supercooled liquids.<sup>35,49</sup>

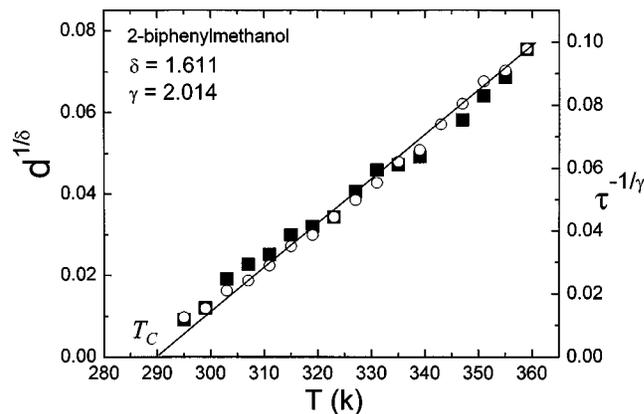


FIG. 3. For illustration of the difference between the liquid crystals and supercooled liquids, the scaling plots for the amplitude of the von Schweidler power law decay,  $d$  (squares, plotted as  $d^{1/\delta}$ ) and for the exponential decay time  $\tau_\alpha$  (circles, plotted as  $\tau_\alpha^{-1/\gamma}$ ) of a supercooled liquid, 2-biphenylmethanol, are shown. The data are from Ref. 35. Both MCT scaling relations are obeyed, but, in contrast to the liquid crystals, there is a single critical temperature,  $T_C$ .

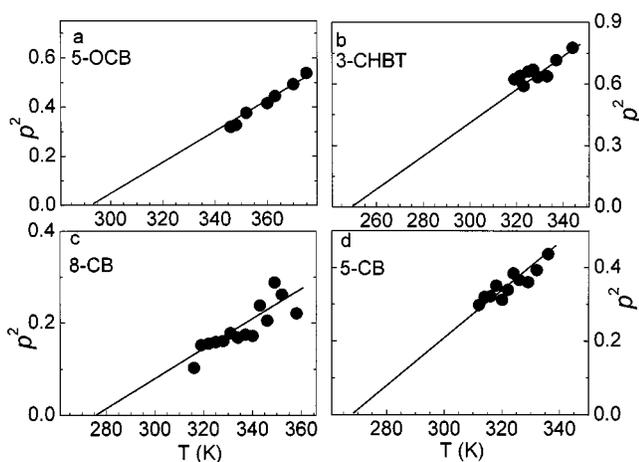


FIG. 4. The temperature dependence of the amplitude of the intermediate power law term,  $p$  (plotted as  $p^2$ ) vs temperature for four liquid crystals. (a) 5-OCB, (b) 3-CHBT, (c) 8-CB, (d) 5-CB. Solid lines are fits to Eq. (5) with  $T_{CL}$  obtained from the fits in Fig. 2, demonstrating that the data obey the MCT scaling relation with critical temperatures,  $T_{CL}$ .

The net result is that the liquid crystal data obeys the same scaling relations as supercooled liquids. However, two critical temperatures are observed, while in supercooled liquids one critical temperature is found for all of the scaling relations. In the liquid crystals,  $T_{CL}$  is found for the scaling relations that apply to the two fast components of the decays.  $T_{CH}$  is found for the scaling relation that applies to the slowest exponential component of the decays.

#### IV. DISCUSSION

LdG mean field theory provides a very useful physical picture that gives a starting point for understanding the two glass transitions in liquid crystals.<sup>8</sup> The theory only describes orientation relaxation on the longest time scale where the decay is exponential. In the isotropic phase near  $T_{NI}$ , owing to the large aspect ratio of the nematogens, liquid crystals form pseudonematic domains. These domains have local nematic order over a correlation length  $\xi(T)$  with a lifetime  $\tau(T)$ . The long time scale exponential relaxation is the decay of the local nematic order. The short time scale power law decay and the crossover region, the von Schweidler power law decay, occur on times fast compared to the loss of local nematic order. The short time scale dynamics reflect relaxations on a time scale short compared to  $\tau(T)$  and a distance scale short compared to  $\xi(T)$ . Thus, there are two relaxation regimes: the intradomain relaxation, which is orientationally constrained by the local nematic order, and the domain randomization, which is the decay of the local nematic order parameter. As  $T_{NI}$  is approached from above,  $\xi(T)$  grows and eventually diverges due to the weakly first-order isotropic to nematic phase transition. According to LdG theory, the phase transition leads to the divergence of domain randomization time  $\tau(T)$  as Eq. (6). However the isotropic to nematic transition does not break the translational symmetry. Translational relaxation, both intra and interdomain, are still allowed even in the nematic phase. Thus, the viscosity of a nematic liquid crystals is not infinity, while the viscosity of a glass is. This type of rotation–translation decoupling has also

been reported for some supercooled liquids,<sup>38</sup> and has been viewed as evidence of the existence of domains in supercooled liquids at least very close to  $T_g$ .<sup>70</sup>

With this pseudonematic domain picture in mind, it is possible to develop a description of the two glass transitions in liquid crystals (Figs. 2 and 4). The two transitions reflect the freezing in of local nematic domains at  $T_{CH}$  and the freezing of all relaxation at  $T_{CL}$ .

Schilling and co-workers<sup>44,52</sup> have presented a “molecular MCT,” a MCT theory of relaxation in complex liquids of hard ellipsoids of revolution, which considers both orientational and translational degrees of freedom. This is in contrast to the original MCT which consider spheres, and, therefore, only translational degrees of freedom. In particular, it was found that for molecules with large aspect ratios, the glass transition is driven by the orientational degrees of freedom. The phase diagram for the ideal glass transition in liquids (the MCT  $T_C$ ) becomes more complicated than that of nearly spherical molecules.<sup>52</sup> There is one transition line that corresponds to the conventional glass transition for spherical particles, which is driven by the cage effect. However, it was shown that for aspect ratios greater than 2.5 (liquid crystals<sup>68</sup>), an additional glass transition line in phase space arises. This transition corresponds to the freezing of the orientational degrees of freedom while translation degrees of freedom are still liquid like to some extent. It is a striking result that this glass transition line is very close to the nematic instability boundary, which indicates that this glass transition occurs near the isotropic to nematic phase transition.

These molecular MCT results and the pseudonematic domain picture can be combined to propose a physical description of the experimental observations presented above. At the orientational glass transition line ( $T=T_{CH}$ , if temperature is the control parameter) a glass phase is formed in which the relative orientations of the pseudonematic domains (as defined by the direction of the local director<sup>71</sup>) are frozen. Within the domains, there are still translational and restricted angular fluctuations, that is, liquid like behavior. However, the orientations of the particles maintain nematic ordered relative to the local director. For length scales  $l \gg \xi(T)$ , that is on macroscopic distance scales, the material is orientationally isotropic because the directions of the local directors are random. However, this pseudonematic orientational glass, the relative directions of the local directors are not evolving in time. This is in contrast to the isotropic liquid phase in which the sample is macroscopically isotropic and the directions of the local directors are continually randomizing. In nematic liquid crystals, this type of pseudonematic orientational glass transition does not actually occur. As the temperature decrease through the isotropic phase, the weakly first-order isotropic to nematic transition takes place at temperature  $T_{NI}$ , which is a few degrees higher than  $T_{CH}$ . The isotropic to nematic transition is the equivalent of crystallization preventing the glass transition. At  $T > T_{NI}$ , however, the pseudonematic orientational glass transition reveals itself through the relaxation dynamics as shown in the scaling relationship of the data in Fig. 2. The fact that the LdG critical temperature  $T^*$  and the critical temperature  $T_{CH}$  are nearly identical seems more than a coincidence. It would be inter-

esting to determine if there is a relationship between the LdG mean field theory and the molecular mode coupling theory.

For time scales shorter than  $\tau_\alpha(T)$ , the intradomain relaxation is the main relaxation channel in the isotropic phase of liquid crystals. Both the short time scale intermediate power law decay and the longer time scale von Schweidler power law decay occur in this time region. The scaling relations shown in Figs. 2 and 4 indicate that crossing from the isotropic phase to the nematic phase does not impose extra restrictions on relaxation on fast time scales. In the picture presented here, crossing the pseudonematic orientational glass transition does not influence the short time dynamics. Complete orientational relaxation cannot occur because of the local nematic order, but translational and orientational dynamics that preserve the local nematic order can still take place. In the context of MCT, upon further cooling, all relaxation will eventually freeze at  $T_{CL}$ , the conventional MCT ideal glass transition. In fragile supercooled liquids, the MCT critical temperature  $T_C$  is typically 20%–30% higher than the experimental glass transition temperature  $T_g$ . Dielectric relaxation experiments on 5-CB indicate that the glass transition temperature is 210 K.<sup>72,73</sup> Comparing  $T_g$  with  $T_{CL}$  for 5-CB, one finds that  $T_{CL} = 1.28T_g$ , a typical value for fragile supercooled liquids. (Values of  $T_g$  for the other liquid crystals are not available.) Recent analysis of the available data on the  $\alpha$  relaxation time  $\tau_\alpha(T)$  in various glass forming liquids showed that at  $T_C$ ,  $\tau_\alpha(T)$  is of the order of  $10^{-6}$ – $10^{-7.5}$  s.<sup>74</sup> The dielectric relaxation spectra of 5-CB<sup>73</sup> and 8-CB<sup>75</sup> give for these materials  $\tau_\alpha(T_{CL}) = 10^{-6.6}$  s. Again, these values are consistent with the view that for the liquid crystals  $T_{CL}$  is akin to  $T_C$  for supercooled liquids.

Rzoska *et al.*<sup>51</sup> studied the glass forming behavior of the liquid crystal 8-CB with dielectric relaxation experiments and analyzed the data within the framework of molecular MCT. They found a single MCT critical temperature 272 K, which is very close to  $T_{CL} = 276$  K found here and significantly lower than  $T_{CH} = 313$  K. This suggests that linear dielectric relaxation experiments are sensitive to the intradomain dynamics.

## V. CONCLUDING REMARKS

OHD-OKE studies of four liquid crystals in the isotropic phase near the isotropic to nematic phase transition show the signatures of two glass transitions within the context of MCT. The amplitudes of the short time scale intermediate power law and the von Schweidler power law obey scaling relations with a critical temperature  $T_{CL}$ .  $T_{CL}$  is equivalent to the MCT  $T_C$  for supercooled liquids.  $T_{CL}$  is 30–50 K below the isotropic to nematic phase transition temperature  $T_{NI}$  (see Table II) and corresponds to the MCT ideal structural glass transition for a supercooled nematic liquid crystal. In the context of MCT, at  $T_{CL}$  the intradomain dynamics of the pseudonematic domains of the isotropic phase freeze.

The long time scale relaxation ( $\alpha$  relaxation), associated with the randomization of the pseudonematically ordered domains, shows a signature of another glass transition. The relaxation time  $\tau_\alpha$  obeys the MCT scaling relation but with a second glass transition temperature  $T_{CH}$ , which is a few degrees below  $T_{NI}$  (see Table II). At  $T_{CH}$ , the local nematic

order associated with the pseudonematic domains freezes in, in accordance with a recent generalization of MCT to systems of molecules in the form of hard ellipsoids of revolution with large aspect ratios ( $>2.5$ ).<sup>44</sup> The intervention of the weakly first-order isotropic to nematic phase transition at  $T_{NI}$  prevents the actual appearance of such orientationally frozen ensembles of pseudonematic liquid domains. The second glass transition of the local nematic order occurs for nematogens (large aspect ratio molecules). Such molecules have relaxation dynamics that are highly influenced by their orientational degrees of freedom. This type of transition is not found for supercooled liquids with aspect ratios below  $\sim 2.5$ .

In recent studies, we demonstrated that the OHD-OKE data (time derivative of the orientational correlation function) for five supercooled liquids were described by Eq. (1).<sup>35,49</sup> While the observed von Schweidler power law and the  $\alpha$  relaxation are consistent with standard MCT (lowest order singularity), the observation of the intermediate power law from  $\sim 1$  ps to ns is not part of standard MCT but does occur for a special case (endpoint scenario<sup>61–64</sup>). It appears that the intermediate power law is a universal feature of supercooled liquids, at least fragile glass formers. The von Schweidler power law and the  $\alpha$  relaxation obeyed the temperature scaling relations of standard MCT. The intermediate power law obeys a temperature scaling relation found for the end point scenario.

In another set of studies it was found that Eq. (1) also describes OHD-OKE data for four liquid crystals in their isotropic phase. For both liquid crystals and supercooled liquids, the decay begins as a power law with temperature independent exponent, has a crossover regime described by another power law with temperature independent exponent, and on the longest time scale, decays exponentially with a highly temperature dependent decay constant. In this paper, we have shown that the liquid crystal power laws and exponential decay constants obey the identical MCT scaling relations as the supercooled liquids. However, in contrast to supercooled liquids, the liquid crystals have two critical temperatures; the higher temperature one associated with the long time scale exponential decay is induced by the isotropic to nematic phase transition. The net result is that supercooled liquids and liquid crystals behave identically except that liquid crystals have a true phase transition and supercooled liquids do not. Here a physical description of the liquid crystal scaling relations and dynamics was presented in terms of the well-established domain structure of liquid crystals. The similarities between the behavior of supercooled liquids and liquid crystals suggest that an underlying domain structure is responsible for the properties of supercooled liquids at all temperatures.

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