

Theory of universal fast orientational dynamics in the isotropic phase of liquid crystals

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A theoretical treatment is presented that demonstrates universal dynamical behavior in the isotropic phase of liquid crystals on ultrafast time scales and short distance scales. The theoretical development generates a temperature independent power law for the short time scale decay of the molecular orientational correlation function. This provides a theoretical rationale for the postulate of universal behavior based on recent experimental observations on two liquid crystal systems. A temperature independent power law decay with the identical exponent, 0.63, was observed for the two systems. First, an alternative theoretical approach reproduces the Landau de Gennes results for the long distance scale, slow time scale orientational dynamics in the isotropic phase. This approach is also capable of examining the short distance scale and short time scale dynamics, and yields a temperature independent power law decay with exponent 0.5. Then critical correlations of fluctuations and local symmetry considerations are included. The Ising model of critical systems is employed. This detailed analysis yields the experimentally observed exponent, 0.63, without recourse to adjustable parameters. Modern theories of dynamic critical phenomena like dynamic scaling theory, the kinetic Ising model and the stochastic model of Kardar–Parisi–Zhang are considered as alternative approaches. While these theories can generate some of the features found in experiment, it is not possible to reproduce the observed experimental results without internal inconsistencies or unwarranted adjustable parameters. © 1995 American Institute of Physics.

I. INTRODUCTION

The isotropic phase of liquid crystals has been extensively studied experimentally and theoretically.^{1–12} In the temperature range somewhat above the nematic to isotropic phase transition, the pretransitional region, there exists substantial orientational order of the liquid crystal molecules. This order extends over a distance scale ξ , the correlation length. The local order has been referred to as pseudonematic domains. As the temperature is lowered toward the isotropic-nematic phase transition, ξ increases. The correlation length tends to diverge at the temperature T^* slightly below the phase transition, T_{ni} . In the nematic phase, orientational order exists over macroscopic distances. In the isotropic phase near T_{ni} , the pseudonematic domains can be large, with correlation lengths of many tens of Å.

The dynamics of the pseudonematic domains on slow time scales (tens of ns) and long distance scales, on the order of ξ , have been studied experimentally and theoretically.^{10,13} Experimental studies have employed the optical Kerr effect^{10,13} to induce an orientational anisotropy into the sample. It is found that this anisotropy decays as a single exponential with a decay rate constant that is highly temperature dependent. As T_{ni} is approached from above, the decay slows dramatically. It tends to diverge and becomes very large at the phase transition. This can be understood in terms of the correlation length of the pseudonematic domains. On a distance scale less than ξ , there is pseudonematic order with an associated local director. The slow time scale exponential is the decay of the orientational correlation of the pseudonematic domains. As the temperature is lowered, ξ grows, and the time for the decay of the orientational correlation increases. At the isotropic-nematic phase transition, this time

diverges; in the nematic phase long range orientational correlation is maintained indefinitely.

de Gennes extended the Landau theory of the second order phase transitions to the weakly first order nematic-isotropic phase transition^{1,2} to analyze the slow time scale and long distance scale dynamics of pseudonematic domains. The Landau–de Gennes (LdG) theory correctly describes the temperature dependence of the exponential decay of the orientational dynamics in the pretransitional region.^{1,10} Some of the LdG results are given below.

In this paper we present a different theoretical approach to the description of the orientational dynamics in the isotropic phase of liquid crystals. This approach, which is based on well established theoretical concepts and methods, is capable of describing the fast time scale, short distance scale dynamics in the pretransitional phase of liquid crystals as well as recovering the LdG results in the appropriate slow time scale, long distance scale limit. The dynamics are analyzed in terms of the fluctuation modes of the pseudonematic domains. These modes have wave vectors (\mathbf{q}) corresponding to length scales from a molecular size to the domain correlation length. When the long wave length limit is taken, the LdG results are obtained. When the sum is performed over \mathbf{q} for large $|\mathbf{q}|$ ($|\mathbf{q}|\xi \gg 1$) and critical correlations of fluctuations are ignored, the short time scale orientational correlation function decays as a temperature independent power law, $t^{-\alpha}$, with $\alpha=0.5$. However, when a more detail analysis is performed, using the Ising model of critical systems^{14–17} after symmetry considerations and including critical correlations of fluctuations, a temperature independent power law is obtained with $\alpha=0.63$. Thus the theory predicts a universal behavior for the fast times scale orientational dynamics in the isotropic phase of liquid crystals.

The temperature independent power law, $t^{-0.63}$, obtained without recourse to adjustable parameters, is identical to the results of recent experiments. These experiments are the motivation for the theory presented below. To understand the nature of the problem, it is important to give a brief, but relatively complete, description of the experiments and experimental results.

II. A BRIEF DESCRIPTION OF RECENT EXPERIMENTAL RESULTS

Fast time scale orientational dynamics of the liquid crystals 5-cyanobiphenyl (5CB) and N-(methoxybenzylidene)butylaniline (MBBA) in their isotropic phases have been studied recently using the transient grating optical Kerr effect (TG-OKE) technique.^{12,18–20} The TG-OKE experiments were performed over a wide temperature range and examined orientational relaxation from tens of fs to tens of ns. The experiments revealed several interesting features of the dynamics of the orientationally correlated domains and intradomain molecular dynamics. These experiments examined the orientational dynamics over much broader ranges of times and temperatures than had been studied previously. The TG-OKE measurements agreed with previous experiments on the slow time scale (>10 ns) and over the limited temperature range of the earlier studies.^{10,13} The slow time scale orientational relaxation is a single exponential decay that follows the LdG temperature dependence in the pretransitional regime.

The fast time scale orientational relaxation (1 ps to 1 ns) are attributed to intradomain orientational motions. It was found that the intradomain dynamics are independent of temperature and viscosity (η) over wide ranges of η/T although over the same ranges, the orientational relaxation dynamics of the domains themselves, occurring on a much longer time scale (>1 ns), change dramatically. At sufficiently high temperature, both 5CB and MBBA begin to make a transition from a locally ordered liquid to a simple liquid; the slow dynamics start deviating from LdG theory and the intradomain dynamics become temperature dependent. The dynamics within the domains are temperature independent because the local pseudonematic structures are preserved during the relaxation. Thermal fluctuations change the local structures on the much longer time scale of the overall domain relaxation described by the LdG theory.

Figure 1(a) shows a log–log plot of four short time scale data sets of MBBA taken at 52.6, 60.8, 68.5, and 78.2 °C ($T_{ni}=46.9$ °C). Within experimental error, all of the data sets display identical highly nonexponential decays. The decays are viscosity/temperature independent in contrast to the slow dynamics that change by a factor of ~ 170 over this same temperature range. The shear viscosity changes by a factor of 10^3 . The faster dynamics become temperature dependent at ~ 90 °C. This is the same temperature at which the slow dynamics of MBBA begin to deviate from LdG theory, i.e., the temperature range in which the correlation length becomes so small that pseudonematic domains no longer exist. The fast data for 5CB (1 ps to 1 ns) [see Fig. 1(b)] display the same behavior,¹² i.e., they are η/T independent from the phase transition temperature ($T_{ni}=35.2$ °C) up to ~ 70 °C. As

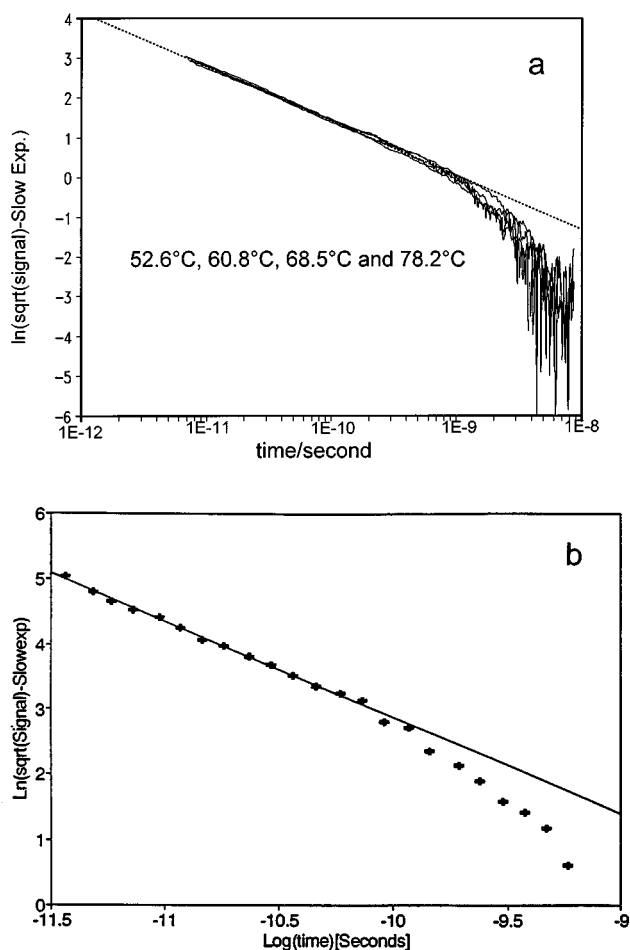


FIG. 1. (a) Fast decay data sets of MBBA at four temperatures (52.6 °C–78.2 °C) are plotted vs time on a log–log plot. The decays are superimposable, showing that the fast MBBA dynamics are viscosity/temperature independent. The dotted line is a straight line through the data showing that the decays obey a power law ($t^{-\alpha}$) with $\alpha=0.63\pm 0.03$. (b) Data taken on the liquid crystal 5CB also display a power law decay with the identical exponent, $\alpha=0.63\pm 0.02$. Both the MBBA and 5CB data are viscosity/temperature independent until the correlation length falls below $3\xi_0$. The striking similarities in the temperature dependent dynamics of MBBA and 5CB may indicate a universal behavior in the isotropic phase of liquid crystals.

long as the correlation length is sufficiently long for pseudonematic domains to exist, as demonstrated by the slow dynamics obeying the LdG theory, the fast intradomain dynamics are η/T independent. This is in spite of the fact that the relaxation times for the slow dynamics change by more than an order of magnitude over the temperature ranges of LdG theory applicability in both MBBA and 5CB. Thus, the fast, intradomain dynamics are not coupled to the hydrodynamic modes, and the results indicate that the dynamics are strongly influenced by the pseudonematic domain structure.

As can be seen in Fig. 1(a), for times shorter than 1 ns, the data fall on a straight line, corresponding to a power law decay of the response function

$$G(t) = G_0 t^{-\alpha}.$$

From the data, α is 0.63 ± 0.03 . The 5CB data [Fig. 1(b)] is also a power law with $\alpha=0.63\pm 0.02$. Thus, qualitatively and quantitatively, the orientational relaxation dynamics in the

isotropic phases of both liquid crystals, MBBA and 5CB, are identical. The fast dynamics in both systems exhibit *power law behavior with the same exponent*, 0.63, and the slow dynamics in both systems begin to deviate from LdG behavior at the same correlation length, $\sim 3\xi_0$, where ξ_0 is on the order of a molecular length.⁹ When the correlation length becomes less than $3\xi_0$, the fast dynamics in both systems become temperature dependent. The remarkable similarities in the dynamical behavior of these systems suggested the existence of a universal principle that governs the dynamics in the pretransitional isotropic phase of liquid crystals and motivated the theoretical treatment presented in the next sections.

Dynamics observed in TG-OKE experiments start with an anisotropy induced in the sample by the two crossed fs excitation pulses. The coupling of the radiation field to the molecules involves stimulated Raman scattering excitation of a subset of the modes of the liquid, i.e., librational modes^{21–25} of the molecules. These essentially harmonic motions are modes of the potential surface arising from the fixed local structure of the liquid that exists on the ultrashort time scale of the excitation pulses. The laser excited librations add to the isotropic distribution of thermally excited librations, making the ensemble of excited librations anisotropic. The initial ultrafast transient (~ 100 fs) seen in TG-OKE experiments consists of a rise in the signal as the overdamped librators begin to undergo angular displacement and the partial decay of the signal as the librational motion dephases and damps. In a dense liquid, coherent motions of pairs, triplets, etc., of molecules can also be driven to some extent and will lead to a very short lived contribution to the signal through interaction induced polarizabilities.^{26,27}

In a crystal, stimulated Raman scattering excites optical phonons. Because of the well-defined lattice structure, damping of the optical phonons returns the molecules to their original positions, leaving no residual anisotropy. In a liquid, damping of the optically excited librations can result in orientational displacements from the initial isotropic configurations. This leaves a longer lived residual orientational anisotropy that will decay by some form of orientational relaxation.

The long range correlation of initially excited librations is determined by the fringe spacing of the transient grating (grating wave vector). Librational damping (dephasing) depends on the local molecular environment. Therefore, spatial variations in orientational correlation extend to high q (short distance scales) following librational damping (hundreds of fs). Thus the relaxation of the residual anisotropy on time scales greater than ~ 1 ps occurs over a broad range of q 's that extend from the molecular length scale ($q \sim 0.1 \text{ \AA}^{-1}$) to the grating fringe spacing ($q \sim 2.5 \times 10^{-4} \text{ \AA}^{-1}$). The theoretical development presented in the following sections examines the influence of fluctuations over the full range of q on the orientational dynamics in the pretransitional isotropic phase of liquid crystals.

III. THEORY

The isotropic-nematic phase transition of liquid crystals is an important example in a chemical system in which criti-

city is superimposed on a weak first order transition.⁹ A small but finite entropy change, characteristic of the first order transition, is observed at the nematic-isotropic transition temperature T_{ni} , where a sharp transition in the system's symmetry occurs. The heat capacity shows divergence at T^* slightly below T_{ni} . This is a characteristic feature of second order thermodynamic criticality. Many pretransitional phenomena are observed in the isotropic phase of nematic liquid crystals.⁹ They are explained as critical behavior, and orientational correlation is identified as the order parameter. The physical origin of critical anomalies is the increase in the correlation length of the order parameter on approaching the critical temperature from above. The increase in the range of correlated regions leads to a corresponding increase in the time scales for dynamic processes (critical slowing down).²⁸ The correlation extends over distances that are increasingly long and times that are much longer than those associated with the dynamics of microscopic elements of the system. Anisotropic intermolecular interactions and correlation of fluctuations cause cooperativity in the alignment of the permanent dipole moments of the liquid crystal molecules.

The order parameter, which is useful for the description of order–disorder transitions, can be identified for any critical transition. The order parameter makes it possible to formulate a unified description of the order–disorder transitions in many different critical systems.^{29,30} The local orientational order in the isotropic phase of a nematic liquid crystal is characterized by a microscopic scalar order parameter, S ,

$$S = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle, \quad (1)$$

where θ is the angle between the axis of the rodlike molecule and the reference direction, the director.^{1,31} This is the same definition that is used to define the order parameter in the nematic phase. In the nematic phase, $S \neq 0$ on a macroscopic distance scale. In the isotropic phase, $S = 0$ on a macroscopic distance scale. However, on a distance scale of $\leq \xi$, $S \neq 0$. If the local order possesses some axial symmetry, one of the symmetry axes can be chosen as the director about which S has the highest value. For local nematic order, it is the local nematic axis. In the isotropic phase of a nematic liquid crystal, a macroscopic symmetric traceless tensor order parameter of rank 2, \mathbf{Q} , is used to describe the anisotropy of thermodynamic properties, e.g., magnetic and dielectric anisotropy.⁹ The elements of \mathbf{Q} are determined by the values of the microscopic order parameter.⁹

A. Theory without including critical correlations of fluctuations

Landau–de Gennes theory provides a good description of the phase transition in the pretransitional region. de Gennes extended the Landau theory of the second order phase transitions to the weakly first order nematic-isotropic phase transition.^{1,2} LdG theory describes the slow time scale, long distance scale dynamics in the isotropic phase. Landau–de Gennes theory as applied to liquid crystals defines the free energy as an expansion in powers of the order parameter. By neglecting the spatial variation of the director and the order parameter, the free energy is expanded as

$$F_n = F_i + AS^2 - BS^3 + CS^4, \quad (2)$$

where F_n is the free energy of the nematic phase, F_i is the free energy of the isotropic phase, A , B , C are constants, and S is the microscopic order parameter. Since the nematic-isotropic transition is a weak first order transition, the magnitude of B is small. A is inversely proportional to the birefringence when the sample is in a magnetic field, and goes to zero on approaching the transition temperature from above,^{1,9}

$$A = a(T - T^*)^\gamma. \quad (3)$$

In this manner, the system produces large fluctuations in the order parameter near the temperature T^* with minimum expense to the free energy. This is the thermodynamic origin of pretransitional phenomena. T^* is the temperature where a second order phase transition should occur, but it is actually slightly below the nematic-isotropic transition temperature, T_{ni} . For systems where mean field theory is valid, the susceptibility critical exponent $\gamma \approx 1$.⁹

To describe the fast time scale, short distance scale dynamics, it is necessary to expand on the considerations employed by de Gennes to describe the isotropic phase. The spatial variations of the local alignment contribute to the free energy through terms involving spatial derivatives of the order parameter. In the isotropic phase, these terms are important for fast time scale dynamics that occur on short distance scales. The total free energy in the isotropic phase can be expressed in terms of the fluctuations of the macroscopic order parameter Q ,⁹

$$F = F_0 + \sum_{\alpha\beta\gamma} A(Q_{\beta\gamma})^2 + L(\partial_\alpha Q_{\beta\gamma})^2, \quad (4)$$

where α , β , γ are indices referring to the laboratory reference frame and $\partial_\alpha = \partial/\partial x_\alpha$. F_0 is the free energy at the minimum. L is the elastic constant in the isotropic phase; its magnitude is smaller than in the nematic phase and is only weakly dependent on temperature. The fluctuations can be expanded in terms of fluctuation normal modes,

$$Q(\mathbf{r}, t) = \sum_{\mathbf{q}} Q(\mathbf{q}, t) e^{i\mathbf{q}\cdot\mathbf{r}}. \quad (5)$$

For simplicity the indices are omitted. Thus, the free energy associated with the fluctuations of the order parameter at wave vector \mathbf{q} is

$$f_{\mathbf{q}} = (F - F_0)_{\mathbf{q}} = A Q_{\mathbf{q}}^2(t) + L q^2 Q_{\mathbf{q}}^2(t). \quad (6)$$

$Q_{\mathbf{q}}$ can be expressed in terms of a microscopic order parameter $S_{\mathbf{q}}$ which describes the molecular orientational order on various distance scales,

$$S_{\mathbf{q}} = \langle S \rangle_{\mathbf{q}}, \quad (7)$$

where the averaging is performed over a distance scale of $|\mathbf{q}|^{-1}$. The relaxation of a fluctuation is determined by the slope of the free energy surface on the relevant distance scale. Then

$$\frac{\partial S_{\mathbf{q}}}{\partial t} \propto \frac{\partial Q_{\mathbf{q}}}{\partial t} = -\frac{1}{2\eta_{\mathbf{q}}} \frac{\partial f_{\mathbf{q}}}{\partial Q_{\mathbf{q}}} = -\Gamma_{\mathbf{q}} Q_{\mathbf{q}}. \quad (8)$$

$\eta_{\mathbf{q}}$ is a viscosity coefficient on the corresponding length scale. The normal modes are chosen such that $Q(\mathbf{q}, t)$'s are uncorrelated, and their time dependencies are separable. For a parabolic surface, the time evolution is exponential with a decay constant $\Gamma_{\mathbf{q}}$. From Eqs. (6) and (8),

$$\Gamma_{\mathbf{q}} = \frac{1}{\eta_{\mathbf{q}}} (A + Lq^2). \quad (9)$$

In the isotropic phase, just above the phase transition, there are regions of orientationally correlated molecules. In the LdG theory the correlations have an Ornstein-Zernike form⁹

$$\langle S(0)S(r) \rangle \approx \frac{1}{r} \exp\left(\frac{-r}{\xi}\right); \quad (10)$$

ξ is the correlation length, and r is the distance. Above the critical temperature, this form of the correlation function is good for $r \gg \xi$.^{15,16} ξ is related to the constants L and A , $\xi = (L/A)^{1/2}$.⁹ From Eq. (3), it is possible to see the manner in which the temperature dependence of the correlation length shows critical behavior⁹

$$\xi = \xi_0 \left(\frac{T^*}{T - T^*} \right)^{\gamma/2} \quad (11)$$

de Gennes identifies ξ_0 as a molecular dimension. Experiments by Courtens,^{4,5} Chu *et al.*,^{6,7} and Stinson and Litster⁸ have determined ξ_0 and found it to be in the range 5.5–7 Å. This is comparable to the cube root of the molecular volume (~ 8 Å) of a liquid crystal molecule such as MBBA. For comparison the molecular length of MBBA is 18 Å.

Introducing $\xi = (L/A)^{1/2}$ into Eq. (9), the dispersion formula for $\Gamma_{\mathbf{q}}$ is obtained,

$$\Gamma_{\mathbf{q}} = \frac{L}{\eta_{\mathbf{q}}} (q^2 + \xi^{-2}). \quad (12)$$

At short distances where $q\xi \gg 1$, the relaxation depends on the fine structure of free energy surface, and $\Gamma_{\mathbf{q}} = Lq^2/\eta_{\mathbf{q}}$. This is what we refer to as intradomain relaxation, the fast orientational dynamics. These dynamics have not been investigated previously. Results of the TG-OKE experiments discussed in Sec. II provide a detailed picture of the intradomain dynamics. L is weakly dependent on temperature, and the viscosity at high wave vector and high frequency is temperature independent.^{28,32} A fundamentally important point is that for large wave vectors, both L and $\eta_{\mathbf{q}}$ are independent of q .^{9,32} As will be shown below, Eq. (12) and the q independence of L and $\eta_{\mathbf{q}}$ for large q lead to the temperature independence of the fast time scale dynamics.

For $q\xi \ll 1$, orientational relaxation depends only on the critical length ξ , and the relaxation time obtained from Eq. (12) is

$$\tau = \Gamma_0^{-1} \propto \frac{\eta(T)}{(T - T^*)^\gamma}. \quad (13)$$

$\eta(T)$ is the long distance scale, bulk viscosity, which is highly temperature dependent. Thus the LdG result of critical divergence for the slow time scale relaxation is recovered. This slow relaxation can be visualized as orientational diffusive randomization of the pseudonematic domains. In the

LdG model of liquid crystals, γ calculated from Eq. (13) has been found to be ~ 1 ,¹⁶ indicating the validity of the application of mean field theory for the *slow orientational dynamics* of the domains.⁹ [In the general theory of critical phenomena, the correlation length exponent and the “critical slowing down” exponent are referred to as ν and νz , respectively; z is the dynamic critical exponent. The general scaling relations do not necessarily follow the LdG relations among the exponents (see Sec. IV).] It has been found experimentally that $3\xi_0$ is the minimum correlation length domain size for which the LdG theory applies.¹⁶ At higher temperatures, the correlation length drops below this value, and the isotropic phase approaches the behavior of a normal liquid.

While the slow time scale isotropic phase orientational relaxation is a single exponential with the temperature dependent decay constant given in Eq. (13), as discussed in Sec. II, the short time scale orientational relaxation is a temperature independent power law decay with exponent, 0.63. The fast orientational relaxation is dominated by large q contributions (intradomain dynamics). *Mean field theory does not apply*, and as will be shown below, the slow time scale scaling of exponents also fails in this regime.

The TG-OKE response function $G(t)$ is related to the spatial Fourier components of the time correlation of the order parameter fluctuation,

$$G(t) \propto \sum_{\mathbf{q}} G(\mathbf{q}, t) = \sum_{\mathbf{q}} \langle Q(\mathbf{q}, t) Q^*(\mathbf{q}, 0) \rangle \\ = \sum_{\mathbf{q}} \langle Q(\mathbf{q}) Q^*(\mathbf{q}) \rangle \exp(-\Gamma_{\mathbf{q}} t). \quad (14)$$

Since

$$\langle Q(\mathbf{q}) Q^*(\mathbf{q}) \rangle = \tilde{G}(\mathbf{q}) \\ = \int d^D \mathbf{r}_{12} \langle Q(\mathbf{r}_2) Q^*(\mathbf{r}_1) \rangle e^{-i\mathbf{q} \cdot (\mathbf{r}_2 - \mathbf{r}_1)},$$

therefore,

$$G(t) \propto \sum_{\mathbf{q}} \tilde{G}(\mathbf{q}) \exp(-\Gamma_{\mathbf{q}} t). \quad (15)$$

For $t < t_0$, the sum in Eq. (15) depends on the q 's sampled. For $t > t_0$, the system is ergodic. Consider the slow dynamics first. For $t > t_0$, only one distance scale, ξ , becomes important as suggested by criticality and the relaxation occurs at distance scales corresponding to $\mathbf{q} \ll \mathbf{q}_0$; where $|\mathbf{q}_0| = (2\pi/\xi)$, the wave vector for the correlation length, ξ . At distances larger than ξ , the spatial correlation varies slowly with distance and therefore,

$$\tilde{G}(\mathbf{q} \ll \mathbf{q}_0) \sim \tilde{G}(\mathbf{q}_0) = \text{const.} \quad (16)$$

This yields a single exponential slow orientational relaxation of the pseudonematic domains

$$G_{>}(t) \propto \sum_{\mathbf{q} \ll \mathbf{q}_0} \tilde{G}(\mathbf{q}) \exp(-\Gamma_{\mathbf{q}} t) \propto \exp[-\Gamma_0(T)t]. \quad (17)$$

This is the hydrodynamic regime described by LdG theory which gives $\Gamma_0(T)$ [Eq. (13)].

For $t < t_0$,

$$G_{<}(t) \propto \int_{q_c}^{q_m} dq q^2 \tilde{G}(\mathbf{q}) \exp(-\Gamma_{\mathbf{q}} t), \quad (18)$$

where q_m is the inverse of the molecular length scale and q_c corresponds to the inverse of an average correlation length over the entire time scale of intradomain relaxation. From the equipartition theorem and the expression for $f_{\mathbf{q}}$ at large q [Eq. (6)], one finds $\tilde{G}(\mathbf{q}) = (k_B T / L q^2)$. For large q , L and η_q are q independent.^{9,32} $\Gamma_{\mathbf{q}} = L q^2 / \eta_{\infty}$ [Eq. (12)], where η_{∞} is the large q and high frequency viscosity which, in addition to being q independent, is also temperature independent.³² Considering the relative values of q_c and q_m , an analytical expression can be obtained by making the reasonable approximation of extending the limits of integration to $q_c = 0$ and $q_m = \infty$,

$$G_{<}(t) \propto \frac{k_B T}{L} \int_0^{\infty} dq \exp[-(L/\eta_{\infty}) q^2 t], \quad (19)$$

$$G_{<}(t) \propto \frac{k_B T (\pi \eta_{\infty})^{1/2}}{2L^{3/2}} t^{-1/2}. \quad (20)$$

This analysis yields a universal power law time decay with a temperature independent exponent of 0.5. The prefactor in Eq. (20) is only temperature dependent through $k_B T$ since η and L are temperature independent on a short distance scale. The prefactor shows that the amplitude of the decay is temperature dependent. However, in an actual TG-OKE experiment, this temperature dependence would not be expected to be observed. The details of the temperature dependence of the coupling of the radiation field to the sample and the damping of librations to produce the residual anisotropy (the observable) have not been considered. The result given in Eq. (20) is universal because the derivation does not depend on the details of the intermolecular interactions. However, the difference between the calculated and the measured value of the exponent is real since the error bars on the data are very small. The more detailed analysis given in the next section resolves this difference.

B. Theory including critical correlations of fluctuations

In the calculation above we have ignored the correlations of fluctuations that occur in a critical system. Since the experimental system shows critical behavior, the critical correlations of fluctuations are important. In the neighborhood of $T = T_c$, the Fourier transform of the two point spatial correlation function in a critical system is of the form¹⁶

$$\tilde{G}(\mathbf{q}) = \langle Q(\mathbf{q}) Q^*(\mathbf{q}) \rangle = \frac{f(q\xi)}{q^{2-\eta}}, \quad (21)$$

where η is the spatial correlation critical exponent whose value depends on the dimensionality of the system; ξ is the correlation length; $f(z)$ is some function of a single variable, and it tends to a finite limit as $z \rightarrow \infty$. At $T = T_c$, $\xi \rightarrow \infty$ and therefore

$$\tilde{G}(\mathbf{q}) \sim q^{-2+\eta}. \quad (22)$$

At $T > T_c$, for $q\xi \gg 1$ (inside the domains)

$$\tilde{G}(\mathbf{q}) \sim q^{-2+\eta} \quad (23)$$

as $f(q\xi) \rightarrow \text{constant}$. This implies that on the short distance scale ($r < \xi$) the spatial correlation function behaves as if the correlation length is infinite. Therefore above T_c , on a distance scale smaller than the correlation length, behavior characteristic of critical phenomena will be observed. This is responsible for the existence of domains with nematic order in the isotropic phase of liquid crystals. On a distance scale short compared to ξ and on a time scale fast compared to the LdG relaxation of the local domain structure, the system exhibits properties characteristic of the nematic phase, and the correlation function $\tilde{G}(\mathbf{q}) \propto q^{-2+\eta}$. Exact calculations of η have been done only for one dimensional and two dimensional Ising models,¹⁴⁻¹⁶ and for higher dimensions various approximate models and computational techniques¹⁵⁻¹⁷ have been developed with limited success.

Using $\tilde{G}(\mathbf{q}) \propto q^{-2+\eta}$ and substituting in Eq. (15) and Eq. (18) we obtain

$$G_{<}(t) \propto \sum_{\mathbf{q}} q^{-2+\eta} \exp(-\Gamma_{\mathbf{q}}t), \quad (24)$$

$$G_{<}(t) \propto \int_{q_c}^{q_m} dq q^2 (q^{-2+\eta}) \exp(-\Gamma_{\mathbf{q}}t). \quad (25)$$

Direct x-ray evidence for antiparallel local ordering in the isotropic phase of 5 CB has been reported by Leadbetter *et al.*¹¹ This is consistent with pseudonematic domains exhibiting local nematic order. Thus, there exists uniaxial (C_{∞}) symmetry about the local director. Because of the uniaxial symmetry, the order parameter variation inside the domain also will be symmetric about the director; the spatial variation of the order parameter is the same in any axial plane containing the symmetry axis of the domain. If the axis of the polar coordinates is chosen along the director, orientational fluctuations will involve the fluctuation of both the angles θ and φ of the molecular axis. However, the order parameter depends on only θ , and the θ fluctuations conserve the axial symmetry of the order parameter about the local director. [While the φ fluctuations do not conserve the symmetry, they also do not affect the order parameter (see Fig. 2).] This means that, inside the domain at any instant of time, the two point orientational correlation, $\langle S(\mathbf{r}_1)S(\mathbf{r}_2) \rangle$, will be the same as the correlation $\langle S(\mathbf{r}_1)S(\mathbf{r}'_2) \rangle$ which is in the axial plane containing \mathbf{r}_1 and the director; \mathbf{r}'_2 is the mapping of \mathbf{r}_2 onto the \mathbf{r}_1 axial plane. [$\mathbf{r}_1 \equiv (r_1, \theta_1, \varphi_1)$; $\mathbf{r}_2 \equiv (r_2, \theta_2, \varphi_2)$; $\mathbf{r}'_2 \equiv (r_2, \theta_2, \varphi_1)$ (see Fig. 3).] Thus, the correlation of the order parameter between any two points is the same as the correlation between two points in the same axial plane.

Since the θ variation in each axial plane is primarily determined by the interactions in that plane, *each axial plane can be considered as a critical subsystem of reduced dimensionality of two. The correlation function in each axial plane will therefore behave like that of a two dimensional critical system.*

Because of the axial symmetry, the three dimensional critical system is reduced to a set of many two dimensional subsystems. Although we have to perform the ensemble av-

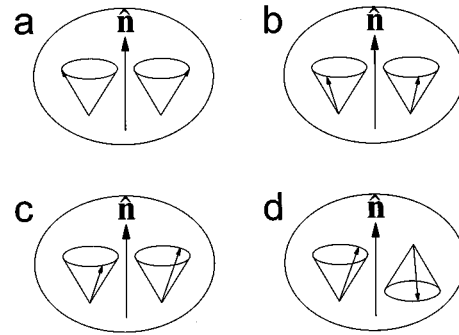


FIG. 2. Order parameters and the θ fluctuations of the axis of the molecules are symmetric about the director $\hat{\mathbf{n}}$, but the φ fluctuations are not symmetric. In configuration (a) both the molecular alignment and the order parameter are symmetric about $\hat{\mathbf{n}}$. In configurations (b), (c), and (d) the molecular alignments are not axially symmetric, but the order parameters are. Configuration (d) illustrates that the order parameter does not change if the molecular axis points up or down. The small arrow on the cone represents the molecular axis. The cones represent the probable range of φ fluctuations for a fixed value of θ corresponding to a particular value of the order parameter.

erage over three dimensions, we need a critical exponent, η , for a two dimensional critical system to use in Eqs. (24) and (25).

Application of the two dimensional Ising model. Since the Hamiltonian is invariant to φ , the orientational interaction energy between molecules 1 and 2, U_{12} can be written as^{10,33}

$$U_{12} = -\lambda S_1 S_2, \quad (26)$$

where λ is a positive constant with the dimension of energy; $S_i = \frac{1}{2}(3 \cos^2 \theta_i - 1)$, where θ_i is the angle between the local director and the molecular axis of the i th molecule. Further, we can make the problem discrete by restricting the possible values of S_i to its limiting values $-1/2$ and 1 , corresponding to $\theta=90^\circ$ and $\theta=0^\circ$, respectively. An average of these two values with suitable weights is mathematically equivalent to

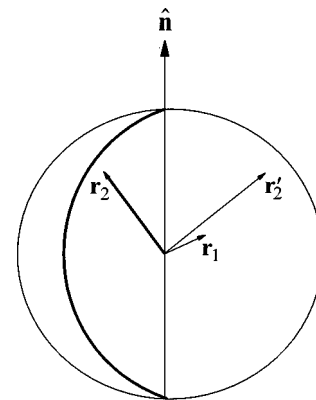


FIG. 3. Consider two distinct axial planes of a pseudonematic domain containing $\mathbf{r}_1 (r_1, \theta_1, \varphi_1)$ and $\mathbf{r}_2 (r_2, \theta_2, \varphi_2)$. $\hat{\mathbf{n}}$ is the director of the domain and also the chosen axis of the polar coordinates. $\mathbf{r}'_2 (r_2, \theta_2, \varphi_1)$ is the mapping of \mathbf{r}_2 onto the \mathbf{r}_1 axial plane. Since the order parameter is symmetric about $\hat{\mathbf{n}}$, the correlation of the order parameter $\langle S(\mathbf{r}_2)S(\mathbf{r}_1) \rangle = \langle S(\mathbf{r}'_2)S(\mathbf{r}_1) \rangle$. Thus the correlation of the order parameter between any two points is the same as the correlation between two points in the same axial plane.

any of the possible continuous values of S_i . The problem is now analogous to that of a two dimensional Ising spin system. The two dimensional Ising model has been solved exactly.¹⁴ The calculated critical exponent for the spatial correlations of the two dimensional Ising spin system will be employed. Ising models for square and triangular lattices have been found to produce the same critical exponents.¹⁴ In those exact calculations, only short range interactions are considered. The lack of dependence on the lattice structure suggests that the exponent is not very sensitive to the exact details of the spatial arrangement in two dimensions. The fact that pseudonematic domains exist down to very short correlation lengths ($\xi \cong 3\xi_0$) suggests that the important interactions are short range. Therefore, it is not unreasonable to use the critical exponent for the two dimensional Ising model. η for the two dimensional Ising model is 0.25.^{14,15} The correlation function behaves like a two dimensional Ising model because the orientational distribution in each axial plane is determined solely by in-plane interactions. The symmetry in the hydrodynamic and critical regime being different, the value of η deviates from the three dimensional mean field value. Therefore,

$$\tilde{G}(\mathbf{q}) = \langle Q(\mathbf{q})Q^*(\mathbf{q}) \rangle \propto q^{-2+0.25}. \quad (27)$$

For a finite correlation length, the correlation function diverges at $q=0$. So the expression for the correlation function in Eq. (24) is not valid for $q=0$ at $T \gg T_c$.¹⁶ We can nonetheless perform the integral in Eq. (25) by considering the limiting case of $q_c=0$ and $q_m=\infty$ as the integrand is still bound. Although the correlation function $\tilde{G}(\mathbf{q})$ is same as the two dimensional Ising system, it must be emphasized that the sum in Eq. (24) must be performed over all the modes of the system which is three dimensional. A sum over all the two dimensional axial planes constituting the domain implies that a three dimensional integral must be used. Using the two dimensional Ising model correlation function and substituting the expression for the high q limit Γ_q from Eq. (12), we obtain

$$G_{<}(t) \propto \int_0^\infty dq q^2 (q^{-2+0.25}) \exp(-\Gamma_q t), \quad (28)$$

$$\propto \int_0^\infty dq q^{0.25} \exp[-(L/\eta_\infty)q^2 t], \quad (29)$$

$$\propto \frac{1}{2} \left(\frac{\eta_\infty}{L} \right)^{0.625} t^{-0.625}. \quad (30)$$

The final result is a temperature independent power law time decay with an exponent 0.625. *This is identical to the measured value, 0.63, within the significant figures of the measurement.* If our ansatz [Eq. (27)] for the correlation function is valid for all nematic liquid crystals, then the calculated temperature independent power law decay is universal. For static critical properties, Ising models give more accurate values for critical exponents than the Landau–de Gennes model.^{15,16} The Landau–deGennes model gives $\eta=0$. Using this value in Eq. (27) would result in a power law exponent of 0.5 as obtained in Eq. (20) using a different approach.

In addition to obtaining agreement with experiment, the results potentially have another importance. It is consistent with the fact that *the fast time scale, short distance scale dynamical properties of a critical system, like long time scale^{34,35} and static^{15,16} critical properties, may depend only on general features* like the dimensionality, D , of the space, the dimensionality, n , of the order parameter, and the symmetry of the interactions, but do not depend on the details of the interactions. To our knowledge, this theoretical approach explains for the first time the fundamentally new experimental results briefly described in Sec. II and establishes the possibility of universal aspects of the dynamics of a critical system on an ultrafast time scale.

IV. OTHER THEORETICAL METHODS

In the treatment given above, we used well known theoretical concepts combined with knowledge of the symmetry properties and distance scales associated with the system to obtain a detailed description of the fast time scale dynamics. The approach also yields the LdG results for slow time scale dynamics. It is important to consider application of other methods to this problem. In the literature, one finds that dynamic scaling theory,^{34,35} the kinetic Ising model,^{36–44} quantum field theory⁴⁵ and stochastic models like that of Kardar–Parisi–Zhang (KPZ) (Refs. 46,47) have been applied to the understanding of critical dynamics. The idea of universality class in dynamic critical phenomena is based on dynamic scaling concepts.^{34,35} Theoretically a large number of dynamic universality classes could be observed for one static universality class.⁴⁵ There has been considerable recent progress in theories of dynamic critical phenomena, but work is still continuing. In this section, the application of these modern theories to the problem of the observed ultrafast dynamics of isotropic phase of liquid crystals will be considered, and some of the difficulties will be explicated.

Dynamic scaling theory states that the Fourier transformed space–time correlation function in a critical system follows the scaling law:³⁴

$$C_\xi^Q(\mathbf{q}, \omega) = 2\pi [\omega_\xi^Q(\mathbf{q})]^{-1} C_\xi^Q(\mathbf{q}) f_{q\xi}[\omega/\omega_\xi^Q(\mathbf{q})], \quad (31)$$

where $f_{q\xi}$ is the shape of the frequency spectrum for the q th mode, $C_\xi^Q(\mathbf{q})$ is the mode density, and $\omega_\xi^Q(\mathbf{q})$ is called the characteristic frequency. Q denotes the order parameter and ξ the correlation length of Q . For the case where $C_\xi^Q(\mathbf{q}, \omega)$ is a Lorentzian of width Γ_q for the q th mode, centered about zero frequency, it can be shown³⁴ that

$$\omega_\xi^Q(\mathbf{q}) = \Gamma_q. \quad (32)$$

In the context of dynamic scaling $\omega_\xi^Q(\mathbf{q})$ can be identified with Γ_q in Eq. (15). In dynamic scaling theory, it is assumed that $\omega_\xi^Q(\mathbf{q})$ is a homogeneous function of q and ξ^{-1} ,^{34,35}

$$\omega_\xi^Q(\mathbf{q}) = \Omega_c q^z \Omega^\pm(q\xi), \quad (33)$$

with different functions above and below T_c (indicated by \pm). It is assumed that at T_c the characteristic frequency is unique,³⁵ i.e.,

$$\Omega^+(\infty) = \Omega^-(\infty) = 1. \quad (34)$$

For a nematic liquid crystal, the characteristic frequency is found to be independent of q in the hydrodynamic regime ($q\xi \ll 1$),

$$\omega_{\xi}^Q(\mathbf{q} \approx 0) = \tau_0^{-1} \alpha (T - T^*) / \eta(T). \quad (35)$$

In the critical regime ($q\xi \gg 1$), the fast dynamics in isotropic nematic liquid crystals are temperature independent, therefore $\omega_{\xi}^Q(q)$ must be independent of temperature and must not depend on ξ . For a continuous transition from the hydrodynamic to the critical regime, the appropriate homogeneous scaling function is

$$\Omega^+(q\xi) = [1 + (q\xi)^{-z}]. \quad (36a)$$

To introduce the observed viscosity dependence we assume,

$$\Omega_c = \Omega_0 / \eta_q; \quad (36b)$$

η_q is the q -dependent viscosity and Ω_0 is independent of temperature, q and ξ . Thus for $q\xi \ll 1$ and $q \approx 0$, the critical slowing down can be obtained from Eqs. (36a) and (36b),

$$\tau_0^{-1} = \Gamma_0 = \omega_{\xi}^Q(\mathbf{q} \approx 0) = \Omega_c \xi^{-z} \alpha \Omega_0 (T - T^*)^{\nu z} / \eta(T), \quad (37)$$

where ν is the correlation length critical exponent and $\eta(T)$ is the bulk viscosity. Similarly, in the critical regime ($q\xi \gg 1$),

$$\Gamma_q = \omega_{\xi}^Q(\mathbf{q}) = \Omega_c q^z = (\Omega_0 / \eta_{\infty}) q^z; \quad (38)$$

in the high q limit η_{∞} is independent of temperature and q . Substituting Eq. (38) in Eq. (28), an expression for the power law exponent can be obtained,

$$\alpha = \frac{1 + \eta}{z}. \quad (39)$$

The observed temperature dependence of the slow orientational dynamics of the domains suggests that $\nu z = 1$ or $z = 1/\nu$. The well known mean field values of the critical exponents in three dimensions are $\eta = 0$, $\nu = 0.5$ and thus from Eq. (39), $\alpha = 0.5$. It shows that the mean field theory does not apply to intradomain dynamics.

It is tempting to use the computational results from Monte Carlo simulations⁴⁸ of the three dimensional Ising model, $\eta = 0.037$ and $\nu = 0.63$, in Eq. (39) in order to obtain a better value of $z = 1.587$ and $\alpha = 0.65$. In this way a power law exponent within error of the experimental value of 0.63 is recovered without violating the dynamic scaling theory. However, experimental results do not support the dynamic scaling argument since the experimental ν is quite different. Stinton and Lister⁸ performed an independent measurement of the correlation length critical exponent ν for MBBA in the isotropic phase and observed the mean field value of $\nu = 0.5$. Susceptibility measurements also confirmed the three dimensional mean field value of $\gamma = 1$ for nematic liquid crystals in their isotropic phase.⁹ In order to be compatible with the conventional theory of critical slowing down, the scaling $z = 2 - \eta$ is appropriate for a nonconserved order parameter.³⁵ In the mean field limit, this relation holds true for the slow orientational dynamics of the domains but it is not compatible with the fast intradomain dynamics. The dynamic scaling argument clearly fails for the fast intradomain

dynamics, and in order to obtain the experimentally observed power law exponent, one has to treat both η and z as adjustable parameters. As adjustable parameters, no physical basis can be found for a legitimate choice of η and z .

Next some specific models will be considered where z has been actually computed. Exact calculations of z have been possible only in the one dimensional model^{36,49} and in the context of mean field theory.⁵⁰ Computation of z for a model without conserved densities often employs the kinetic Ising model (or Glauber model).^{36,41} The field theoretical estimate gives $z = 2$ in three dimensions.^{51,52} If we have to use the three dimensional η , the value of z required to obtain the experimentally observed power law exponent is far from this estimate. In two dimensions different calculations yield values of z in the range 1.75 (the exact lower bound) $\leq z \leq 2.3$ and values of η between 0.2 and 0.3.^{41,53} Therefore the choice of z and η is not unique, and to obtain the experimentally observed power law, one has to treat them as adjustable parameters. Renormalization group theory approaches to the kinetic Ising model have been attempted on fractal lattices with no success in obtaining a general relation between dynamic and static exponents. For some specific fractal geometries, different values of the dynamic exponent z are obtained; $2d_f$, $d_f + 1/\nu$, and $1 + d_f$ (d_f and ν are, respectively, the fractal dimension and the correlation length exponent).^{54,55} Therefore, it is not surprising that in the case of systems with nonconserved order parameter, the dynamic exponent bears no simple relation to static exponents and dynamic scaling applied to slow dynamics may breakdown for ultrafast dynamics in the critical regime.

Slow time scale stretched exponential and power law behavior have been derived with the dynamic Ising model.⁴²⁻⁴⁴ In these cases, the stretched exponential and the power law exponents are dependent on temperature and not universal as they are dependent on the critical point (T_c). The fastest power law calculated in three dimensions is with an exponent 0.065 for $\pm J$ interaction distribution.⁴³ Until now, whenever dynamic scaling theory, the kinetic Ising model, and the stochastic model of KPZ are applied to calculations of explicit time dependence, they are limited to much slower dynamics that are really macroscopic, e.g., kinetics of interface roughening during crystal growth⁴⁶ and dynamics of domain growth during spinodal decomposition in block copolymer melts.⁴⁷

These methods, briefly discussed above, cannot yet describe the fast dynamics in the isotropic phase of liquid crystals. The approach in Sec. III B considers the symmetry of the order parameter fluctuation and the Hamiltonian for orientational interaction. These give rise to a spatial correlation which is the same as that of an exactly solved model (the two dimensional Ising model). The results reproduce the experimentally observed temperature independent power law with no adjustable parameter. While the theoretical approach presented in this paper is not as general as other theoretical methods, it is useful for the specific problem of intradomain dynamics of the isotropic phase of nematic liquid crystals. Our approach is equivalent to having $z = 2$ (field theoretical result in three dimensions) and $\eta = 0.25$. (η is allowed to deviate from the three dimensional mean field value in the

critical regime where the dynamic scaling fails.)

The question remains; why does the universal behavior on a fast time scale relate to critical exponents other than those observed for the slow time scale, long distance scale behavior. The slow time scale universal behavior is associated with the IR fixed point in renormalization group (RG) flow of the Hamiltonian.^{45,56} We speculate that it is possible on a fast time scale (in the nonergodic limit) different fixed points exist and therefore create the possibility of observing different universal behavior not predicted by conventional theories of critical phenomena or dynamic scaling theories. The results of the femtosecond TG-OKE experiments indicate that on a fast time scale, the interactions confined to the axial planes of a domain may lead the RG flow to a fixed point which is the same as in the two dimensional Ising model. Now if there is very weak interactions present between the axial planes, they are insignificant on a fast time scale, but they will grow slowly with renormalization. At sufficiently long time, crossover to an equilibrium fixed point occurs, and the slow, long distance scale dynamics obey mean field scaling which is different from the two dimensional Ising model.⁵⁶ If this speculation is correct, different classes of critical behavior associated with the "other" fixed points might be explored by ultrafast measurements.

V. CONCLUDING REMARKS

We have presented a theoretical treatment of the fast time scale, short distance scale orientational dynamics in the isotropic phase of liquid crystals. Because the nematic isotropic transition is a critical transition, in the isotropic phase, on a distance scale short compared to the correlation length, the local structure is like that of the nematic phase. This permits the theoretical concepts of critical phenomena to be applied to the analysis. Uniaxial symmetry of the pseudone-matic domains reduces the three dimensional system to a set of two dimensional subsystems. The Ising model of two dimensional critical systems is used. The results yield a temperature independent power law time decay with exponent 0.625, in exact agreement with experimental observation without recourse to adjustable parameters. These results should also have implications for dynamics in the nematic phase on fast time scales. The development depends on the wave vector independence of the elastic constant and the viscosity on short distance scales and the uniaxial symmetry of the system. These are also features of the nematic phase and, particularly on a fast time scale, the problem would be similar. In actual experiments, the problem may become more complicated since the nematic phase is very susceptible to surface effects that are not important in the isotropic phase. Wave vector dependent variation of the director and second order variation of the order parameter may need to be considered.

This work displays a universal character for the fast dynamics in the isotropic phase of liquid crystals. It may be of more general significance because it demonstrates that concepts of critical behavior can be applied to ultrafast time dependent phenomena. The theoretical approach presented in this paper may seem deceptively simple, yet it is successful and fully consistent with the molecular picture of liquid crys-

tals. It would be interesting and important to show that the rigorous application of more general theoretical methods can reproduce the experimental results without unwarranted adjustable parameters.

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