Dynamics of Fluctuations below a Stationary Bifurcation to Electroconvection in the Planar Nematic Liquid Crystal N4

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We fitted $C(\mathbf{k}, \tau, \epsilon) \propto \exp[-\sigma(\mathbf{k}, \epsilon)\tau]$ to time-correlation functions $C(\mathbf{k}, \tau, \epsilon)$ of structure factors $S(\mathbf{k}, t, \epsilon)$ of shadowgraph images of fluctuations below a supercritical bifurcation at $V_0 = V_c$ to electroconvection of a planar nematic liquid crystal in the presence of a voltage $V = \sqrt{2}V_0 \cos(2\pi f t)$ [$\mathbf{k} = (p, q)$ is the wave vector and $\epsilon \equiv V_0^2/V_c^2 - 1$]. There were stationary oblique (normal) rolls at small (large) f. Fits of a modified Swift-Hohenberg form to $\sigma(\mathbf{k}, \epsilon)$ gave f-dependent critical behavior for the minimum decay rates $\sigma_0(\epsilon)$ and the correlation lengths $\xi_{p,q}(\epsilon)$.

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Critical opalescence is a familiar phenomenon that occurs, for instance, near liquid-gas critical points and near the phase separation of binary mixtures [1]. It is caused by refractive-index fluctuations due to droplets of fluid of lesser or greater than average density or concentration. The fluctuations are the response of the system to the thermal noise inherent in the Brownian motion of the molecules or atoms. The droplet size increases in proportion to a correlation length ξ that diverges at the critical point. Likewise, the decay rate σ_0 of the droplets vanishes as the critical point is approached. When ξ is sufficiently large, ambient light is scattered and the fluid becomes "milky." Analogous phenomena occur in many spatially extended nonlinear systems as they are driven away from equilibrium and toward an instability, or bifurcation [2–8]. For those cases the length and time scales are more nearly macroscopic, and the fluctuations can be observed with modern shadowgraph techniques [9–11]. Here we present experimental results for ξ and σ_0 for electroconvection (EC) of a nematic liquid crystal (NLC) [12]. For certain parameter ranges the data suggest that the transition in the presence of fluctuations is of first order, although the deterministic theory predicts a second-order transition. Fluctuation-induced first-order transitions are rare, but have been found, for instance, for the nematic-smectic-A transition in liquid crystals [13], in the microcrystallization of di-block copolymers [14], and for the onset of Rayleigh-Bénard convection [7,15,16].

A NLC consists of elongated molecules that align locally relative to each other [17]. The alignment direction is called the director $\hat{n}$. When a NLC is confined between parallel glass plates with a small spacing d between them, $\hat{n}$ is influenced by the interaction of the molecules with the surfaces. We used surfaces that caused alignment in a unique direction parallel to the plates (planar alignment). This breaks the rotational invariance usually found in isotropic liquids, for instance, in Rayleigh-Bénard convection [7,15,16]. We applied a voltage $V = \sqrt{2}V_0 \cos(2\pi f t)$ between transparent indium-tin oxide electrodes on the inner surfaces of the confining plates. This induced a transition (or bifurcation) at $V_0 = V_c$ from a spatially uniform state without flow to a convecting state of lower symmetry. The bifurcation is expected to be supercritical [18], analogous to a critical point in a two-dimensional equilibrium system, e.g., to a Curie point of a ferromagnet. Here we report on the effect of fluctuations on the bifurcation to EC.

When fluctuations are small, one may neglect their interactions and discuss them in terms of a linear theory (LT) [19–21]. Then we expect that $\xi \sim |\epsilon|^{-\nu}$ with $\nu = 1/2$ and $\sigma_0 \sim |\epsilon|^{\lambda}$ with $\lambda = 1$. Here $\epsilon \equiv V_0^2/V_c^2 - 1$ [18]. When the fluctuations become larger, nonlinear terms lead to interactions between them. Then several universality classes of critical behavior exist for equilibrium systems, determined primarily by the dimensionality of the system and by the number of components n of the order parameter. For two-dimensional equilibrium systems one has primarily Ising systems ($n = 1$) and $X - Y$ systems ($n = 2$). It is

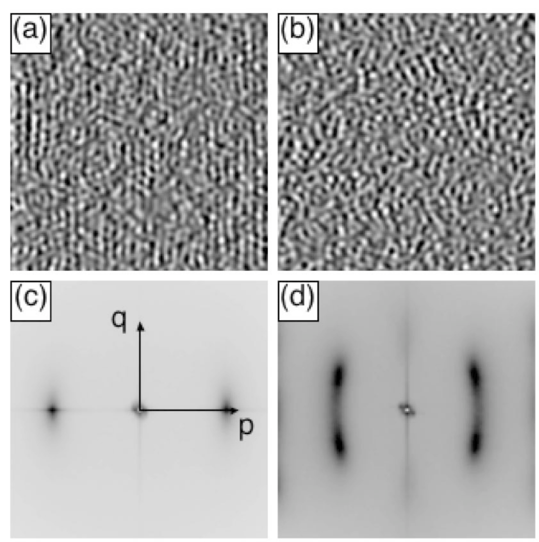

FIG. 1. (a),(b) Shadowgraph images of size 0.88×0.88 mm^2 for $\epsilon = -1.1 \times 10^{-3}$. (a) $f = 4000$ Hz. (b) $f = 25$ Hz. (c),(d) The central part $-7.2 \leq p, q \leq 7.2$ of the averaged structure factor $S(\mathbf{k})$ based on 4096 images for $\epsilon = -1.1 \times 10^{-3}$. (c) $f = 4000$ Hz. (d) $f = 25$ Hz. The director is horizontal.

not certain that this classification carries over in direct analogy to nonequilibrium cases.

The range of ϵ over which fluctuation interactions become important depends on the coupling of the thermal noise to the system. For EC, the relevant parameter is the ratio of the thermal energy to a characteristic elastic energy of deformation $F = k_B T/\bar{k}d$ ($\bar{k}$ is an average elastic constant of the NLC) [2]. On the basis of a Ginzburg-like criterion [22] one can estimate that the critical region is encountered near $\epsilon_c \simeq F^{2/3}$. For the NLC used by us, one finds $\bar{k} \simeq 10^{-11}$ N [23], and, thus, for a cell with $d \simeq 25\ \mu$m, one has $\epsilon_c \simeq 6 \times 10^{-4}$. For much larger ϵ the prediction of linear theory should pertain.

To our knowledge ϵ_c or the universality class should not depend on f. As shown in Figs. 1(a) and 1(c), at large $f = 4$ kHz we found "normal" stationary convection rolls in the fluctuations below and the patterns above onset. Their wave vectors are parallel to $\hat{n}$. For the fluctuations we found $\lambda \simeq 1$, consistent with LT. However, the correlation lengths gave $\nu = 0.40 \pm 0.03$, which differs from $\nu = 1/2$ of LT. Perhaps this exponent is an effective exponent representing data in a crossover region from linear to critical behavior. However, then one would have to argue either that the crossover region is different for ξ and σ_0 or that the value of λ is not altered measurably by fluctuation interactions.

At small $f = 25$ Hz the fluctuations, as well as the patterns above onset, correspond to oblique stationary rolls with their wave vectors forming an oblique angle $|\theta| > 0$ with $\hat{n}$ [Figs. 1(b) and 1(d)]. There are two degenerate modes with angles $\pm\theta$. Here the critical behavior was qualitatively different. No power law could describe the results for σ_0 and ξ. Both quantities, although they initially changed upon approaching V_c, deviated from a power law for $|\epsilon| \lesssim 0.02$ and approached a constant value rather than diverging. These results differ from the critical behavior of equilibrium systems, but are consistent with a first-order transition in the presence of noise sufficiently strong to prevent hysteresis.

We took shadowgraph images [9–11] $\tilde{I}_i(\mathbf{x}, \epsilon)$ [$\mathbf{x} = (x, y)$ are the spatial coordinates in units of the cell thickness d] of a cell with $d = 25\ \mu$m and filled with the NLC Merck N4 (a eutectic mixture of two azoxy compounds, CH3O-C6H4-NO=N-C6H4-C4H9 and CH3O-C6H4-N=NO-C6H4-C4H9) doped with 0.1% by weight of tetra butylammonium bromide. We used the same $0.88 \times 0.88\ \text{mm}^2$ area of a sample for all measurements. The temperature was constant within 2 mK near 30 °C. The alignment was planar. The conductance was $6.2 \times 10^{-7} (\Omega\,\text{m})^{-1}$ at 30 °C, $f = 25$ Hz, and $V_0 = 2.0$ V. It increased by 8% when f was increased to 4 kHz, and decreased by about 16%/yr. Measurements on other samples show that these changes have no significant effect on the results. We used the total shadowgraph power P above V_c, equal to the variance of the images in physical space, to determine that the bifurcation was nonhysteretic and stationary over the range $25 \leq f \leq 8000$ Hz. We found $V_c = 6.04(11.49)$ V for $f = 25(4000)$ Hz [24]. For $V > V_c$ the pattern consisted of stationary oblique (normal) rolls for $f < f_L \simeq 1.3$ kHz ($f > f_L$). At each voltage we waited 300 s, and then took 4096 shadowgraph images 0.3 to 1 s apart, depending on ϵ.

From each image we calculated $I_i(\mathbf{x}, \epsilon) \equiv \tilde{I}_i(\mathbf{x}, \epsilon)/\tilde{I}_0(\mathbf{x}, \epsilon) - 1$. Here $\tilde{I}_0(\mathbf{x}, \epsilon)$ is a background image obtained by averaging 4096 images at the same ϵ. For each $I_i(\mathbf{x}, \epsilon)$ we derived the structure factor (the square of the modulus of the Fourier transform) $S_i(\mathbf{k}, \epsilon)$ and averaged 4096 $S_i(\mathbf{k}, \epsilon)$ to get averaged structure factors $S(\mathbf{k}, \epsilon)$, where $\mathbf{k} = (p, q)$ is the wave vector. Figures 1(c) and 1(d) show examples. At low frequencies [1(d), $f = 25$ Hz] two pairs of peaks correspond to two sets of rolls oriented obliquely to the director. At high frequency [1(c), $f = 4$ kHz] only one pair of peaks corresponding to normal rolls was observed.

Figure 2 shows time series for $f = 25$ and 4000 Hz of $S(\mathbf{k_0}, \epsilon, t)$ for $\epsilon = -0.010$ at $\mathbf{k} = \mathbf{k}_0$ where $S(\mathbf{k}, \epsilon)$ has a maximum. The fluctuations have a random appearance and are of similar size at both frequencies. In Fig. 3 we show the autocorrelation function $C(\mathbf{k}, \tau) = \langle S(\mathbf{k}, t) S(\mathbf{k}, t + \tau)\rangle_t / \langle S(\mathbf{k}, t) S(\mathbf{k}, t)\rangle_t$ of the data illustrated in Fig. 2 on linear scales. The inset gives the same data on a semilogarithmic plot. The correlations decayed exponentially in time. A fit of $Ae^{-\sigma\tau}$ to the data yielded $\sigma = 0.14\ \text{s}^{-1}$ for $f = 25$ Hz and $0.22\ \text{s}^{-1}$ for $f = 4000$ Hz. Although $S(\mathbf{k})$ differs from the structure factor of the refractive index by a k-dependent factor $\mathcal{T}(k)$ [11], we note that $C(\mathbf{k}, \tau)$, and thus σ, are not influenced by $\mathcal{T}(k)$.

Decay rates at $\epsilon = -0.010$ are shown in Figs. 4(a) and 4(c) for oblique ($f = 25$ Hz) and in Figs. 4(b) and 4(d) for normal ($f = 4$ kHz) rolls along two lines parallel to the p and q axes and passing through the maxima of $S(\mathbf{k})$ at $\mathbf{k}_0$. The Swift-Hohenberg forms

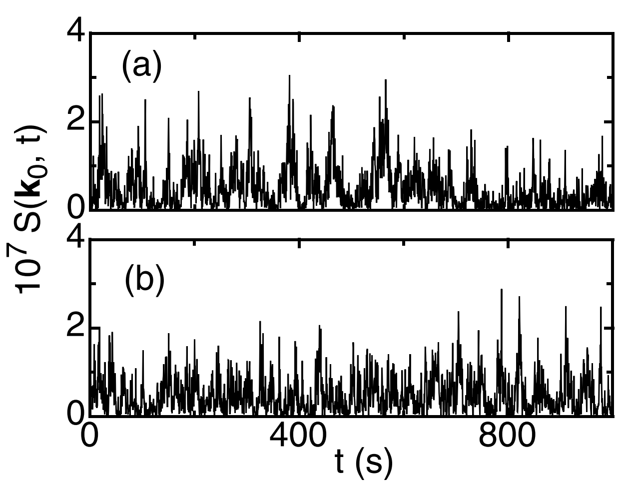

FIG. 2. Parts of the time series of length 2048 s of $S(\mathbf{k}_0, \epsilon, t)$ at $\epsilon = -1.0 \times 10^{-2}$ for (a) $f = 25$ Hz, $\mathbf{k}_0 = (3.936, 1.968)$, and (b) $f = 4000$ Hz, $\mathbf{k}_0 = (4.830, 0)$.

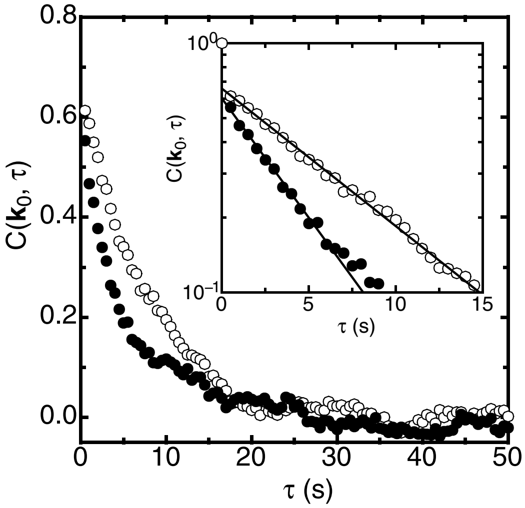

FIG. 3. The time autocorrelation function of the fluctuations of the structure factor at $\epsilon = -1.0 \times 10^{-2}$ for $\mathbf{k}_0 = (3.936, 1.968)$ at $f = 25$ Hz (open circles) and for $\mathbf{k}_0 = (4.830, 0)$ at $f = 4000$ Hz (solid circles).

$$\sigma(p, q_0) = \sigma_0(\epsilon) \times [\xi_p^2(p^2 - p_0^2)^2 + 1] \qquad (1)$$

with $q_0 = 1.968$ and

$$\sigma(p_0, q) = \sigma_0(\epsilon) \times [\xi_q^2(q^2 - q_0^2)^2 + 1] \qquad (2)$$

with $p_0 = 3.757$ were fit to the data in 4(a) and 4(c). From 4(c) one sees that a parabola, restricted to either positive or negative q, would not provide a good fit. The large-f results in Fig. 4(b) were fitted by Eq. (1) (solid line). However, for the normal rolls we used [25]

$$\sigma(p = 0, q) = \sigma_0(\epsilon) \times (\xi_{q2}^2 q^2 + \xi_{q4}^2 q^4 + 1) \qquad (3)$$

in 4(d) (solid line).

Each fit yielded a value at a given ϵ of the minimum decay rate $\sigma_0(\epsilon)$, and of the correlation length $\xi_p(\epsilon)$ or $\xi_q(\epsilon)$. For $f = 4$ kHz we plot ξ_p and σ_0 as a function of $|\epsilon|$ in Figs. 5(a) and 5(b), respectively. Fits of power laws to the results for $|\epsilon| < 0.05$ yielded $\nu = 0.40 \pm 0.03$ and $\lambda = 0.92 \pm 0.06$. The result for λ is reasonably consistent with the prediction of linear theory and suggests either that the critical region has not been reached in this experiment or that fluctuation interactions do not alter λ by a measurable amount. The result for ν differs significantly from the LT prediction. Perhaps the values of $|\epsilon|$ are too *large* for LT to apply, but in that case the range of applicability would have to be different for ξ_p and σ_0. Thus the data suggest, but do not firmly establish, a deviation of the critical behavior from LT.

In Figs. 6(a) and 6(b) we show analogous results for $f = 25$ Hz. Here the situation is quite different. For $|\epsilon| \lesssim 0.02$ deviations from LT are noticeable for σ_0, ξ_p, and ξ_q. A power law does not fit the data. The results suggest that all three parameters approach a finite value at $\epsilon = 0$. This differs from that of any known equilibrium system near a critical point. However, it would be consistent with a first-order phase transition in the presence of strong noise.

We also measured the total power $P = \int_0^\infty S(\mathbf{k}) d^2k$ at various $\epsilon < 0$, and found that the $|\epsilon|$ dependence of P depended on f. Correlation lengths derived from the widths of $S(\mathbf{k})$ agreed with those reported here. At small f we also found that the maximum of $S(\mathbf{k})$ remained finite,

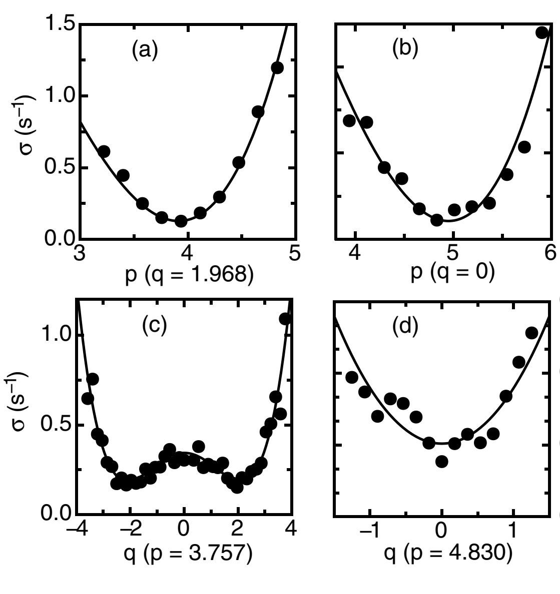

FIG. 4. The decay rates $\sigma(p, q, \epsilon)$ as a function of p and q at $\epsilon = -1.0 \times 10^{-2}$ for (a),(c) $f = 25$ Hz and (b),(d) $f = 4000$ Hz. The solid lines are fits to the data that yielded (a) $\sigma_0 = 0.13$, $\xi_p = 0.37$, (b) $\sigma_0 = 0.21$, $\xi_p = 0.29$, (c) $\sigma_0 = 0.18$, $\xi_q = 0.21$, and (d) $\sigma_0 = 0.31$, $\xi_{q2} = 0.87$, $\xi_{q4} = 0.11$.

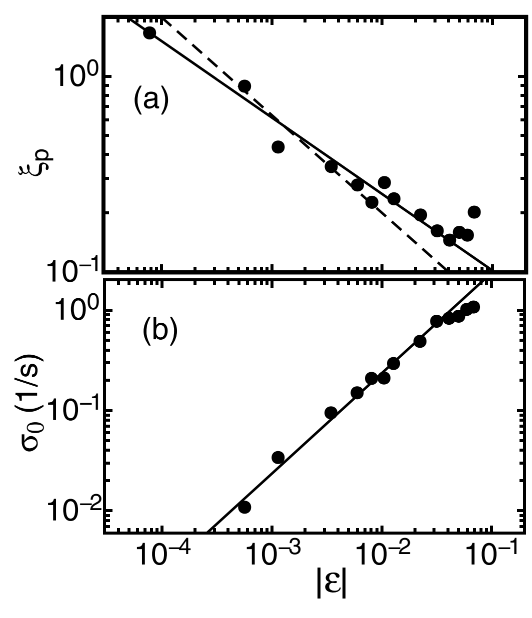

FIG. 5. (a) The correlation length ξ_p and (b) the decay rate σ_0 versus $|\epsilon|$ for $f = 4$ kHz derived from fits of Eq. (1) to $\sigma(p, q = 0)$. Dashed line in (a) $\nu = 1/2$. Solid lines: fits to the data that gave (a) $\nu = 0.40 \pm 0.03$ and (b) $\lambda = 0.92 \pm 0.06$.

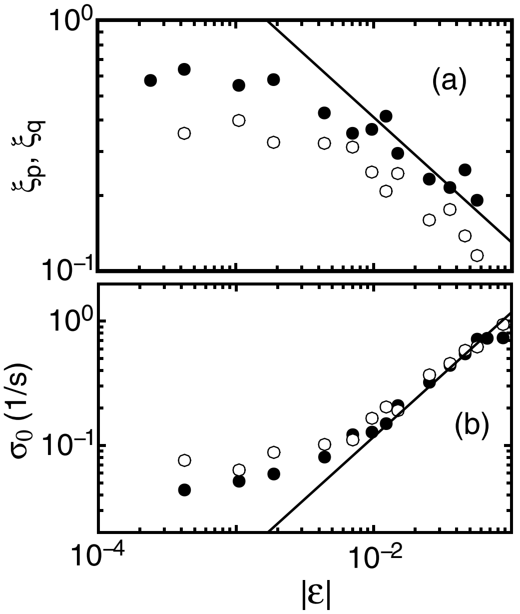

FIG. 6. (a) Correlation lengths ξ_p (solid circles) and ξ_q (open circles) and (b) decay rates σ_0 derived from fits of Eq. (1) to $\sigma(p, q_0)$ (open circles) and Eq. (2) to $\sigma(p_0, q)$ (solid circles) versus $|\epsilon|$ for $f = 25$ Hz. Solid lines: $\nu = 1/2$ and $\lambda = 1$ in (a) and (b), respectively.

whereas one would have expected it to diverge at $\epsilon = 0$ (as it appears to do at large f). This work will be reported in a more detailed publication.

In this Letter we presented measurements of the dynamics of thermally driven fluctuations near the bifurcation to stationary electroconvection of the nematic liquid crystal N4. The results for the decay rate σ_0 and the correlation lengths ξ_p and ξ_q for oblique rolls at small driving frequency f tend toward a constant value at the bifurcation. This differs from the prediction of linear theory which yields power-law singularities with exponents $\lambda = 1$ and $\nu = 1/2$, respectively. It also differs from known possibly relevant equilibrium critical behavior which yields vanishing decay rates and diverging correlation lengths, albeit with modified exponent values. It is consistent with a first-order transition in the presence of strong noise where no hysteresis would be observed. The results for normal rolls at large f are more nearly consistent with LT, although the value of ν is somewhat lower than the predicted value $1/2$.

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