Abstract

In this thesis I study some fundamental aspects of pattern formation in electroconvection of nematic liquid crystals. The system consists of a nematic liquid crystal with negative or only mildly positive dielectric anisotropy sandwiched between two transparent electrodes and aligned planar-homogeneously. Some electric conductivity is needed. When applying an AC voltage and increasing its rms value above a certain threshold, there is an instability leading to a spatially periodic state which can be measured by optical methods. The patterns depend on the material parameters of the nematic, the thickness d of the layer, and on the applied frequency. I treat the case of relatively low frequencies, i.e., the so-called conductive range. The physical model introduced in this thesis should be valid for other cases, too.

A long-standing problem in electroconvection is the Hopf bifurcation leading to travelling rolls, observed in thin cells with relatively low conductivity. The standard hydrodynamic description ("Standard model" SM) going back to Helfrich where the nematic is treated as an anisotropic ohmic conductor, always predicts a stationary bifurcation leading to stationary rolls. Also the inclusion of additional effects like flexoelectricity has up to now not improved the situation. Similarily, the small hysteresis observed in very sensitive experiments in some parameter ranges cannot be understood with the standard description, which always predicts a continuous bifurcation.

This gave rise to develop and explore in this thesis a generalization of the SM, the Weak Electrolyte Model (WEM).

In Chapter 2, I review the derivation of the SM with the methods of generalized hydrodynamics. There are several approximations along the path from the "first principles" (the hydrodynamic conservation laws and balance equations, and the microscopic Maxwell equations) to the basic equations of the SM. This chapter is intended to show these approximations.

In Chapter 3, I formulate the WEM. In contrast to the ohmic behaviour assumed in the SM, the WEM describes the conductive properties of the nematic by the dynamics of two species of oppositely charged freely mobile ions. They originate from impurities or dopants by a dissociation-recombination reaction and migrate relative to the fluid, as in usual weak electrolytes, with velocities proportional to their mobilities and proportional to the electric field. The ionic species are assumed to have constant, possibly different, mobility tensors $\mu^{\pm}$ with principal values perpendicular and parallel to the director, $\mu_{\perp}^{\pm}$ and $\mu_{\parallel}^{\pm}$, respectively. Experimental evidence for the relevance of weak electrolytic effects in nematics with long recombination times τ_{rec} actually goes back more than 20 years.

The WEM expresses the total space-charge density, which already appears in the SM, as the difference of the number densities of the two ionic species. In addition, migration leads to a charge separation and gives rise to a new field, which can be expressed in terms of the local conductivity $\sigma_\perp(\boldsymbol{r},t)$ ("charge-carrier mode") proportional to the sum of the number densities weighted with the mobilities $\mu_\perp^+$ and $\mu_\perp^-$. The WEM contains two new dimensionless parameters,

$$\tilde{\alpha} = \sqrt{\frac{\mu_\perp^+ \mu_\perp^- \gamma_1 \pi^2}{\sigma_\perp^{\mathrm{eq}} d^2}}, \quad \tilde{r} = \frac{\tau_d}{\tau_{\mathrm{rec}}} = \frac{\gamma_1 d^2}{K_{11}\pi^2 \tau_{\mathrm{rec}}}.$$

Here, γ_1 is a rotational viscosity, K_{11} the splay constant, d the layer thickness, and $\sigma_\perp^{\mathrm{eq}}$ the conductivity in the equilibrium state. The mobility parameter $\tilde{\alpha}$ is proportional to the geometric mean of the mobilities $\mu_\perp^+$ and $\mu_\perp^-$ and describes the rate at which the charge-carrier mode is excited. The recombination parameter $\tilde{r}$ is the inverse recombination time τ_{rec} in units of the inverse of the director relaxation time τ_d, and describes the relaxation of the charge-carrier mode towards equilibrium $[\sigma_\perp(\boldsymbol{r},t) = \sigma_\perp^{\mathrm{eq}}]$ by the dissociation-recombination reaction.

Apart from the case of very special boundary conditions, the non-convecting (motionless) basic state of the WEM is nontrivial and implies boundary layers of the charge carriers. I investigate these boundary layers in Chapter 4 and conclude that they can be neglected in the relevant experiments. This is an important result since it means that the predictions of the WEM are rather independent of the boundary conditions for the charge carriers, involving, in general, the complicated and unknown electrochemistry of the electrodes. This conclusion is supported by experimental evidence. In addition, the linear and weakly-nonlinear analysis in the following chapters is simplified considerably by this assumption. In the rest of this work, I use physically clean "blocking" boundary conditions where the charge carriers cannot cross the electrodes.

In Chapter 5, I linearize the WEM around the trivial basic state (without boundary layers) using lowest-order expansions for the space and time dependence of all fields. This allows for an analytic approach. The analysis gives the onset of instability and the wavevector and frequency (in the case of the Hopf bifurcation) of the new solution describing a stationary or travelling pattern. The possibility for a Hopf bifurcation can be seen quite easily. A first version of this analysis restricted to normal rolls (roll axis perpendicular to the homogeneous alignment) has been published [1].

The WEM predicts both, Hopf and stationary bifurcations, depending on the parameters. The condition for a Hopf bifurcation is, in a good approximation,

$$C'(\omega_0)\left(\frac{\pi}{d}\right)^3 K_{11}\sqrt{\frac{\mu_\perp^+\mu_\perp^-}{\gamma_1\sigma_\perp^{\mathrm{eq}}}} > \frac{1}{\tau_{\mathrm{rec}}},$$

where the dimensionless function $C'(\omega_0)$ is of order 10. It increases with the external frequency ω_0 of the AC voltage if the dielectric anisotropy is negative, and depends otherwise only on scaled material parameters of the SM. Assuming long recombination times of the order of seconds, this equation explains why travelling rolls are observed for all external frequencies in thin cells and for liquid crystals with a relatively low equilibrium conductivity $\sigma_\perp^{\rm eq}$ [of the order of $10^{-8}(\Omega{\rm m})^{-1}$], while they are observed only for higher frequencies in an intermediate range of $\sigma_\perp^{\rm eq}$ and d. The precise value and the temperature dependence of the recombination time $\tau_{\rm rec}$ are unknown; so no quantitative predictions of the system parameters at the transition from the Hopf bifurcation to the stationary one (codimension-two point) could be made. The experimental findings on the nematics MBBA and I52 (see p. 5 or Ref. 2 for the chemical formula for this compound) were consistent with $\tau_{\rm rec}$ of the order of 10 s.

In the Hopf regime and not too near to the codimension-two point, the recombination effects drop out (one can set $\tau_{\rm rec} = \infty$ in the formulas) enabling a quantitative experimental test of the predicted oscillation frequency of the travelling rolls (Hopf frequency). In this case, the Hopf frequency is given by the left-hand side of the previous equation (see also Eq. (39) in Ref. [1]), i.e., it is proportional to d^{-3}, $(\sigma_\perp^{\rm eq})^{-1/2}$, $C'(\omega_0)$, and to $(\mu_\perp^+\mu_\perp^-)^{1/2}$. Here the geometric mean $(\mu_\perp^+\mu_\perp^-)^{1/2}$ is the only parameter that is not contained in the SM.

Quantitative comparisons with experiments are made for MBBA and I52. For I52, some material parameters of the SM are not known. They were determined by fitting the prediction of the SM to the experimental results for the threshold voltage and the roll angle (with respect to the homogeneous alignment) as function of the AC frequency ω_0 at different temperatures. It is possible to use the SM since it predicts nearly the same threshold and roll angle as the WEM.

Fits to the measured Hopf frequency give values for $(\mu_\perp^+\mu_\perp^-)^{1/2}$ of the order of $10^{-10}{\rm m}^2/({\rm Vs})$ in MBBA and I52, consistent with published data. With $(\mu_\perp^+\mu_\perp^-)^{1/2}$ fitted for each temperature to one data point, the Figures 5.7 - 5.11 (see also Figs. 2a and 2b in Ref. [2]) show for I52, that the difference between the WEM prediction and the measured values differed typically by less than 10% for changes of d^3 by a factor of 8 (two different cells), of $(\sigma_\perp^{\rm eq})^{1/2}$ by a factor of 2.2 (variation of the temperature), and of $C'(\omega_0)$ by a factor of 2.5 (variation of the external frequency). In MBBA, the Hopf frequency increases much faster with ω_0. In the Figures 5.7 and 5.8 it is shown that the WEM predicts this increase nearly quantitatively in a range covering more than a factor of 10. The different behaviour of the two materials is mainly due to the different dielectric anisotropies: $\epsilon_a \approx -0.52$ for MBBA, $\epsilon_a \approx -0.056$ (30°C)$\cdots$0 (60°C) for I52.

The mechanism of the Hopf bifurcation is found to be similar to that of other pattern-forming systems showing a Hopf bifurcation: a primary destabilization feedback mechanism is coupled to a stabilizing second feedback cycle which is here me-

diated by the charge-carrier field, with a slow intrinsic time scale (Figure 5.12). In many aspects, the σ field is reminiscent of the slow concentration field of thermal convection in binary fluid mixtures.

Chapter 6 is devoted to the weakly-nonlinear analysis of the most important contributions of the WEM equations. I calculate approximate analytic expressions of the coefficients of a one-dimensional complex Ginzburg–Landau equation (CGL) describing the dynamics of the envelope (including of course the actual amplitude) of, say, the left-travelling waves. The weakly-nonlinear analysis predicts that the Hopf bifurcation expected for long recombination times $\tau_{\rm rec}$ is always continuous and that the nonlinear saturation is stronger than in the SM (smaller amplitude). Decreasing $\tau_{\rm rec}$, the bifurcation becomes stationary and, in general, also (slightly) hysteretic. For even shorter recombination times, it becomes continuous (Figures 6.4 and 6.5) and in the limit $\tau_{\rm rec} \to 0$, the WEM approaches the SM.

This agrees qualitatively with the experiments on I52. It can be concluded that three different predictions: the amplitude of the nonlinear state after the jump in the stationary-hysteretic regime, the decrease of the oscillation frequency on increasing the voltage in the Hopf regime, and the (linear) condition for a Hopf bifurcation, agree with the experiments assuming a recombination time of 10–20s.

Two experiments with MBBA cells showed a more puzzling behaviour. The linear dynamics assessed by *subcritical* fluctuations is oscillatory, but the deterministic bifurcation seemed to be stationary-hysteretic. I show that the following interpretation is compatible with the WEM: the Hopf bifurcation is actually continuous, but a subsequent jump to a nonlinear state takes place at a value of the control parameter which can not be distinguished experimentally from the threshold value. Recent experiments on the nematic mixture Merck Phase 5 confirm this interpretation.

The oscillatory behaviour (Hopf bifurcation) in the two MBBA eperiments mentioned above was obtained from the correlation function of fluctuations below threshold, which anticipate the linear-deterministic dynamics. The strength of the fluctuations was observed to be (only) 30% to 40% higher than expected from naive estimates based on the equipartition theorem for thermal fluctuations of the director only (without considering charge-density fluctuations). Can this result which indicates that thermal fluctuations are nearly those of an equilibrium system, be understood? To give a better understanding of thermal fluctuations in this (and other hydrodynamic nonequilibrium systems) I apply in Chapter 7 the Landau approach of fluctuating hydrodynamics to the SM equations. The conclusion is that a "generalized equipartition theorem can indeed be applied to the director fluctuations and that charge-density fluctuations indeed contribute in the two experiments only by, respectively, 3% and 10% [3,4]. Using the WEM would lead to a factor of two (two critical left- and right travelling modes instead of one stationary mode) that is cancelled by the correlation time in the denominator of Eq. (7.41), which the WEM

predicts to be twice as long as in the SM. The correlation time, determined in the experiments by the correlation function as well, agrees with the WEM, and not the SM.

A concluding chapter attempts to give some directions for future research. The coefficients for the CGL were derived in this thesis for the most simple case of either left- or right-travelling waves. However, one has to consider the interaction of degenerate critical modes, and, for finite amplitudes, also slowly-relaxing modes excited by the nonlinearities. Coupled equations for these modes can possibly explain quantitatively the spatio-temporal chaos (STC) of *localized* states observed in I52 at lower temperatures. The CGL predicts also a small region where travelling waves are unstable to long-wavelength modulations (Benjamin–Feir instability). It would be fascinating to explain the amplitude-STC of *extended* states observed in I52 at higher temperatures, by a CGL in the Benjamin–Feir unstable range. This would enable a quantitative experimental comparison with the predictions of one of the most simple and generic equations producing STC.

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