Dynamics of Disclinations in Nematic Liquid-Crystal Main-Chain Polymer Films

Jens Rieger*

Theoretische Physik, Universität des Saarlandes, 6600 Saarbrücken, Federal Republic of Germany. *Received July 6, 1989*

ABSTRACT: With observation of the time evolution of the disclination density in nematic films consisting of thermotropic liquid-crystal main-chain polymers, a subsequent decrease of disclination density after sudden heating to the nematic phase has been found.[3,4] Shiwaku et al. and Hashimoto et al. reported that the measured time dependence of the average distance, d, between two adjacent disclinations is fairly well fitted by assuming the scaling relation $d \sim t^{0.35}$, i.e. the disclination density, ρ, should decay as $\rho \sim t^{-0.7}$. We propose a simple mean-field theory, which is based on results for diffusion reaction systems of the type $A + B \rightarrow 0$ where A and B correspond to the two different types of end points of a disclination line, respectively. With our results the measured time dependence of ρ is described slightly better than by the simple algebraic relation since the measured tendency of ln $\rho(t)$ versus ln t toward a convex function is reproduced.

Liquid-crystal main-chain polymers exhibit one or more of the typical liquid-crystal mesophases.[1] Here we are concerned with nematic films of liquid-crystal polymers. In these systems one often finds locally a well-defined nematic structure; i.e., there is a well-defined director on a length scale that is large compared to the longitudinal extension of the polymer but small in comparison with the length probed by light microscopic methods.[2-4] The decay of the nematic order is mainly due to the presence of frozen in disclination lines, which end in topologically singular points of strength (+) and (−), respectively, at the surface of the nematic polymer film.[2] (For a comprehensive review of the topological aspects of disclinations in liquid-crystal phases, see the monograph by Kléman.[5]) The occurrence of disclinations in nematic polymer systems is of some technological importance since these defects diminish—by destroying the global nematic order—the strength of the solidified material.

Shiwaku et al.[3] examined the time behavior of the number of (+), (−) disclination points after sudden heating of solvent-cast liquid-crystal main-chain polymer films to the nematic phase; see also ref 4. These authors measured the root of the mean-squared distance, d, between two adjacent disclinations and found that the data points are sufficiently well described by the scaling law $d \sim t^{0.35}$; i.e., the defect density, ρ, should scale as $\rho \sim t^{-0.7}$. See also Figure 1 where the datas of ref 3 are reproduced.

In the following a theory of the diffusion reaction type will be proposed that attempts to describe the subsequent annihilation of (+) and (−) defects after heating. The physical idea behind the following theory is that a "frozen in" state of disclinations is a nonequilibrium state produced by the formation process of the system. Pairwise annihilation of disclination lines is apparently not realized either due to too high energy barriers to be overcome or due to constraints. Sudden heating of the system provides it with the necessary thermal energy to overcome energy barriers of comparable height and leads to an annealing of the system via pairwise annihilation of disclination lines. This process stops when all barriers of height $\simeq kT$ have been eliminated. Further annealing requires additional heating.

The mathematical assumptions and results of the theory will be explained. Then I shall discuss the shortcomings of the present theory and compare my approach with other current theories on the diffusion-limited reaction problem.

The dynamics of singular end points of disclination lines (≡"defects" of positive or negative strength[6]) are modeled as follows, where the (+) and (−) defects are labeled as A and B particles, respectively: N_0 A particles are distributed in such a way on a regular two-dimensional lattice of M vertices that each A particle defines the center of a square "unit cell" consisting of m_0 lattice points, with $m_0 = M/N_0$. This approach is of the mean-field type and is justified insofar as in experiment no segregation of (+) and (−) defects into domains was observed;[3,4] i.e., on the average one can assign to each (+) defect one neighboring (−) defect. The A particles are immobile in the present model. This assumption is justified because Mazelet and Kléman found[2] that the mobility of (+) defects is much smaller than that of the (−) defects. I further assume that into each unit cell one places randomly one B particle, which diffuses freely until it meets the respective A particle. Upon encounter both particles annihilate. Of course, B particles may also enter adjacent cells. I assume, however, that on the average the energy barrier to be overcome for annihilation of B and A particles is the smallest for the local unit cell the B particle is assigned to and is larger for adjacent cells. The mean-field treatment of time evolution explained below implies then that the larger energy barriers are overcome later. In order to recast the problem into a two particle problem, which can be tackled more simply, I assume periodic boundary conditions for each unit cell. The rate equation for the number of B particles is assumed to have the form

$$dN_B = -K(N_A)\, N_B\, dt \tag{1}$$

where $K(N_A)$ is the rate constant that depends on the number N_A of A particles present in the system; of course, $N_A = N_B$. $K(N_A)$ is proportional to the inverse of the average time, τ, it takes for a $A + B \rightarrow 0$ reaction to occur. Using the method of generating functions, Montroll derived the average number of steps, $\langle n \rangle$, that a B particle, being placed randomly on a generalized d-dimensional torus of size m^d, needs until it meets an A particle fixed at the origin.[7] For the two-dimensional case,

* Current address: BAST AG, Testkörperphysik, Polymerphysik, ZKU/S-G201, 6700 Ludwigshafen, TRG.

0024-9297/90/2223-1545$02.50/0

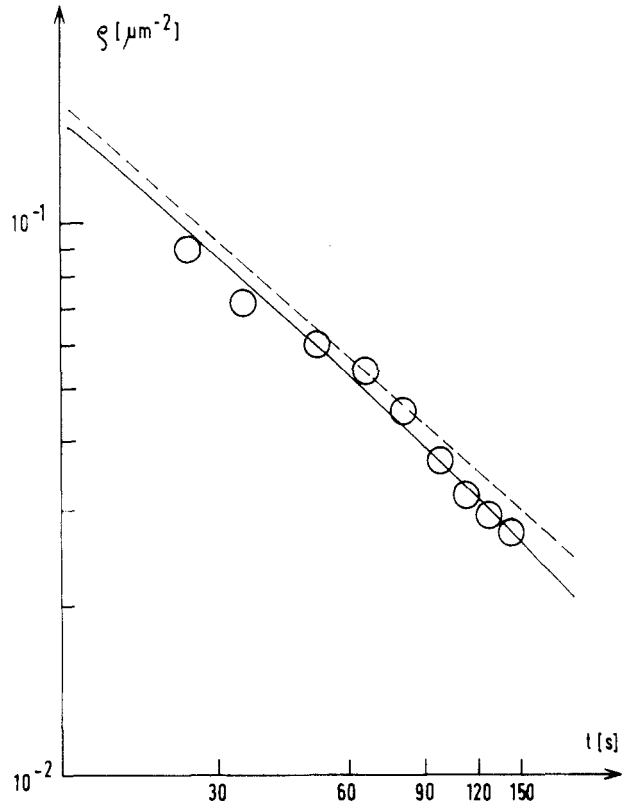

Figure 1. Time dependence of the density ρ of end points of disclination lines in a double logarithmic plot ln $\rho(t)$ vs ln t. The data points are from ref 3, where we used that $\rho = d^{-2}$ (see text). The solid line is drawn according to eq 6. The dashed line represents the algebraic law[3,4] $\rho \sim t^{-0.7}$.

which is interesting in the present context, Montroll found

$$\langle n \rangle = c_1 m \ln m + c_2 m + \ldots \tag{2}$$

where only the leading terms in m have been retained. For the square lattice c_1 and c_2 are given by $c_1 = 0.32$ and $c_2 = 0.2$.[7] I assume now that $\tau \sim \langle n \rangle$; i.e., a B particle jumps with a constant rate randomly to adjacent lattice sites. Furthermore, I set $m = M/N_A$. The latter assumption is again of the mean-field type: it is assumed that each time a A,B pair annihilates the size of the remaining cells scales as the inverse of the actual particle density M/N_A. It can be shown[8] that this approach yields in the one-dimensional case the same asymptotic time behavior of $N_A(t)$ as given by the analytically derived solution.[9] τ can now be given as

$$\tau \sim [c_1 M/N_A \ln (M/N_A) + c_2(M/N_A)] \tag{3}$$

Equation 1 then reads using $K(N_A) = \alpha/\tau$

$$[c_1 M/N \ln (M/N) + c_2 M/N]\, dN = -\alpha\, dt \tag{4}$$

with $N = N_A \equiv N_B$. α is some positive constant that depends on the mobility of the (-) defects. Upon integration eq 4 yields

$$[c_1 + c_2 + \ln (N/M)]/[N/M] = -\alpha t + [c_1 + c_2 + \ln (N_0/M)]/[N_0/M] \tag{5}$$

Trying to compare this result with experiment or related theories, one meets two severe problems: First, in eq 5, t is given as a function of N, instead of $N = N(t)$. Second, and this point is more problematic, in experiment one measures the defect *density*, ρ, i.e., a number of disclination end points per some prefixed area with the dimension of $[\rho] = (\text{length})^{-2}$. In eq 5 one finds the density, $\rho \equiv N/M$, given by a dimensionless number, which is fixed by the assumed—but not specified—size of the unit cells that form the lattice needed in the theory. And it is, of course, not possible to give for $t = 0$ the discrete approach of the real continuum system because, first, too little is known on the microscopic level about the relevant length scales and, second, this approach might fail at all in the limit $t \to 0$ if the system behaves at $t \to 0$ as a *fast* reacting system. Fast means that the A + B $\to$ 0 reaction is *not* diffusion limited but might be of a ballistic nature. It might be annotated that this ρ problem is also found in other fields of physics where one tries to describe continuum models by a lattice approach. In order to be able to compare eq 5 with experiment I circumvent this problem by simply introducing some, unknown, scaling parameter, ζ, defined by $\rho = \zeta N/M$, which is lumped into the constants c_1, c_2, and α, which are suitably redefined. One thus obtains

$$-\frac{a + b \ln \rho}{\rho} + c = t \tag{6}$$

ρ is the measured defect density given as (number of defects)/(μm^2). a, b, and c are phenomenological constants depending on c_1, c_2, ζ, and α, where c_1 and c_2 are known, see above, α is in principle given by the properties of the respective polymer system, and ζ is unknown. As was stated above, eq 6 yields t as a function of ρ and not $\rho(t)$ as one might wish. But by simply interchanging the t-ρ-coordinates of the experimental data given in ref 3, one can fit eq 6 to the data points. The best result is obtained for $a = 0.055$, $b = 1.09$, and $c = -0.17$. The result is shown in Figure 1, where the coordinates are given in the original representation for the sake of clearness. As can be seen from Figure 1 the present approach (eq 6) describes the time dependence of the measured values of ρ slightly better than the algebraic law[3,4] $\rho \sim t^{-0.7}$, insofar as the tendency of the ln $\rho(t)$ versus ln t representation toward a convex function is reproduced. Equation 6 can be assumed to be valid only in an intermediate time range, which here seems to coincide with the range examined in the above-mentioned experiments. For long times a saturation effect should occur since the system must finally exhibit a constant density of thermally activated defects.

A shortcoming of the presented theory is, of course, that long-range interactions between pairs of points have been neglected. Recall that two end points of a disclination line, which are seperated by a distance r, interact via a ln r potential where points of opposite charge attract each other.[10] But the inclusion of these long-range interactions into a theory on diffusion-limited reactions is enormously difficult, and to my knowledge there exist no diffusion reaction theories that are concerned with particle interactions but of the short-range type which I used here.[11] Note, however, that due to $N_A = N_B$ and a more or less random distribution of A and B particles the interaction of an A particle is effective essentially with its neighbors, and for larger distances averages out. Thus the effective interaction is short-range.

Finally, I want to compare my approach with concurring reaction diffusion theories. There are theories[12] that are based on a rate equation of the form

$$dN_B = -K(t)\, N_B\, dt \tag{7}$$

where $K(t)$ depends in some way on a probability density function, $\psi(t)$, for transitions between lattice sites. In the present theory $\psi(t) = \delta(t - \tau_0)$ where τ_0 is the time that a B particle needs for a jump to an adjacent vertex.

When less trivial distributions are used for $\psi(t)$, it is possible to model the randomness of certain physical systems.[12] Our theory differs from theories based on eq 7 since we assume that the rate "constant" depends on time not by a probability density function, $\psi(t)$, for the hopping of particles but by the actual number of existing traps (A particles). That means that we do not consider the reaction diffusion behavior of single particles placed into a random array of traps, but we assume that all particles interact by the fact that each time two particles annihilate the density and thus the surroundings of the (remaining) particles change.

Another attempt has been made during the last years to understand the dynamics of the $A + B \rightarrow 0$ reaction where no rate equation is used as a starting point but where one tries to attack the problem directly; see ref 9 and references given therein. It was found that segregation is an important phenomenon;[13] i.e., there are "domains" where one finds a surplus density of one type of particle (for an illustration of this phenomenon, see, e.g., Figure 5 of ref 13a). It is obvious when regarding the micrographs obtained from nematic main-chain polymer films[3,4] that such a segregation does not take place in these systems. The reason for this apparent discrepancy is that one must indeed include particle interactions that prevent the system from segregation if one attempts to use "direct" theories.

To conclude, I have presented a simple "double" mean-field theory for the description of the decay of the density of disclinations in nematic films of liquid-crystal main-chain polymers. It was found that the present approach, which is based on a generalized form of the rate equation, approximates the functional behavior of the time dependence of the number of disclination points slightly better than an assumed algebraic law.

Acknowledgment. I thank Professor A. Holz for a critical reading of the manuscript. The financial support of the Volkswagen Stiftung is gratefully acknowledged.

References and Notes

(1) See e.g.: (a) Ciferri, A. In *Polymer Liquid Crystals*; Ciferri, A., Krigbaum, W. R., Meyer, R. B., Eds.; Academic Press: London, 1982. (b) Proceedings of the 1st International Conference on Liquid Crystal Polymers, Bordeaux, France, 1987; *Mol. Cryst. Liq. Cryst.* **1987**, *153*; **1988**, *155*.
(2) Mazelet, G.; Kléman, M. *Polymer* **1986**, *27*, 714.
(3) Shiwaku, T.; Nakai, A.; Hasegawa, H.; Hashimoto, T. *Polym. Commun.* **1987**, *28*, 174.
(4) Hashimoto, T.; Nakai, A.; Shiwaku, T.; Hasegawa, H.; Rojstaczer, S.; Stein, R. S. *Macromolecules* **1989**, *22*, 422.
(5) Kléman, M. *Points, Lines and Walls*; Wiley: Chichester, U.K., 1983.
(6) In the crude approach presented here it makes no sense to consider the actual strength, i.e., the value of the modulus of the respective defects. Therefore, only the sign of the defect strength is considered.
(7) Montroll, E. W. *J. Math. Phys.* **1969**, *10*, 753.
(8) Rieger, J., unpublished results.
(9) Doering, C. R.; ben-Avraham, D. *Phys. Rev.* **1988**, *A38*, 3035.
(10) (a) Kosterlitz, J. M. *J. Phys.* **1974**, *C7*, 1046. (b) Jose, J. V.; Kadanoff, L. P.; Kirkpatrick, S.; Nelson, D. R. *Phys. Rev.* **1977**, *B16*, 1217. (c) Nelson, D. R. In *Phase Transitions and Critical Phenomena*; Domb, C., Lebowitz, J. L., Eds.; Academic Press: London, 1983; Vol. 7.
(11) Presently, we seek to determine the influence of long-range interactions between diffusing and reacting particles on $\rho(t)$ via Monte Carlo simulations.
(12) (a) Shlesinger, M. F. *J. Chem. Phys.* **1979**, *70*, 4813. (b) See also the reference list in: Kang, K.; Redner, S. *Phys. Rev. Lett.* **1984**, *52*, 955.
(13) (a) Toussaint, D.; Wilczik, F. *J. Chem. Phys.* **1983**, *78*, 2642. (b) Anacker, L. W.; Kopelman, R. *Phys. Rev. Lett.* **1987**, *58*, 289.