

Frustrated rotations in nematic monolayers

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Abstract. Tabe and Yokoyama found recently that the optical axis in a chiral monolayer of a ferronematic rotates when water evaporates from the bath: the chiral molecules act as propellers. When the axis is blocked at the lateral walls of the trough, the accumulated rotation inside creates huge splays and bends. We discuss the relaxation of these tensions, assuming that a single dust particle nucleates disclination pairs. For the simplest geometry, we then predict a long delay time followed by a non-periodic sequence of “bursts”. These ideas are checked by numerical simulations.

PACS. 61.30.Hn Surface phenomena: alignment, anchoring, anchoring transitions, surface-induced layering, surface-induced ordering, wetting, prewetting transitions, and wetting transitions – 61.30.Jf Defects in liquid crystals

1 Introduction

The chiral compound R(OPOB) (see Fig. 1) forms a bulk ferroelectric liquid crystal. But it can also be deposited as a monolayer on water (or on water glycerol mixtures, which slow down the dynamics). Tabe and Yokoyama observed these layers optically and found that the optical axis of this two-dimensional nematic was rotating continuously in the xy plane [1]. They interpreted this remarkable result in terms of an irreversible process: water evaporation from the supporting liquid is responsible for the molecular precession. They wrote down the basic Onsager relations required to describe the effect. They consist of

a) Two fluxes: the rotation rate Ω and the mass flux of water evaporation J_w .

b) Two forces: the torque τ (around a vertical axis) applied on the nematic molecules by external fields or by local distortions, and the chemical potential difference $\Delta\mu$ between water in the liquid and water in the gas [2].

The entropy source per unit area of the monolayer is then

$$T\dot{S} = \tau\Omega + \Delta\mu J_w \quad (1)$$

and the Onsager relations are

$$\Omega = \gamma_1^{-1}\tau + b\Delta\mu, \quad (2)$$

$$J_w = b\tau + P\Delta\mu. \quad (3)$$

In equation (2), γ_1 is a classical friction coefficient for nematic rotations [3] and P is related to the permeability of

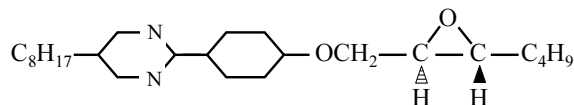


Fig. 1. Chemical structure of R(OPOB).

the air layer above the Langmuir trough. The interesting coupling coefficient is b .

Reference [1] shows that in simple conditions ($\Delta\mu$ is fixed and $\tau \sim 0$), Ω is indeed proportional to $\Delta\mu$, and that the experimental values of b are of the right order of magnitude (typically the rotation periods $2\pi/\Omega$ are a few seconds).

We are interested here in one particular feature —the angle ϕ (labelling the direction of the optical axis in the horizontal plane) is forced by water evaporation to rotate in the monolayer. But at the lateral edges of the trough, the direction is expected to be anchored at the walls [3]. This frustrated situation forces the internal elastic energy (proportional to $|\nabla\phi|^2$) to relax by successive “bursts”. Our aim is to present a simple description of these bursts.

2 Weak and strong anchoring

The basic equation for the director angle $\phi(x, y, t)$ in the monolayer can be derived from equation (2), incorporating elastic torques into τ , and is

$$\frac{\partial\phi}{\partial t} = \frac{K}{\gamma_1}\nabla^2\phi + \Omega, \quad (4)$$

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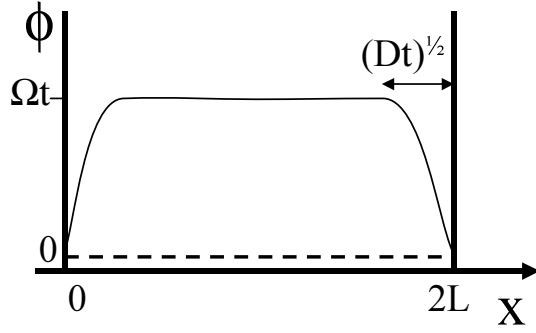


Fig. 2. A nematic monolayer confined by two walls at $x = 0$ and $x = 2L$, with boundary conditions $\phi = 0$ at both ends. At $t = 0$, $\phi = 0$ everywhere, dashed line. After time t has passed and under the influence of equation (4) the profile evolves, solid line.

where Ω is fixed because $\Delta\mu$ is imposed. We have assumed that the splay and bend elastic constants are equal, $K_1 = K_2 = K$. It will be convenient to define a diffusion coefficient

$$D = \frac{K}{\gamma_1}, \quad (5)$$

which we expect to be of order 10^{-6} – 10^{-7} cm^2/s , depending on the water/glycerol fraction.

Frustration originates from the anchoring at the lateral boundaries of the trough. We expect to have an energy per unit length at the boundary of the order $-U \cos(\phi - \beta)$, where β define a preferred orientation (*e.g.* normal to the walls) [4]. When expressed per molecule, the anchoring energy U is small compared to the nematic coupling (maybe 10 times smaller), but it is very important. If we have a gradient $\nabla\phi|_n$ normal to the wall, anchoring ruptures whenever the torque $K\nabla\phi|_n$ becomes larger than U . This corresponds to a critical value of the gradient

$$\kappa_{\text{surf}} = \nabla\phi|_n = U/K \sim 1/10a, \quad (6)$$

where $a \sim 1\text{nm}$ is a molecular size. Thus, we see that $\kappa_{\text{surf}} \sim 10^6 \text{ cm}^{-1}$. Here, we shall be mostly interested in the limit where the gradient $|\nabla\phi|$ is smaller than κ_{surf} , *i.e.*, the strong anchoring limit. Then frustration effects in the interior of the monolayer are important.

3 The role of the dust particle

We shall focus our attention on a simple geometry (see Fig. 2), where the monolayer is limited by two parallel walls separated by distance $2L$. The boundary conditions are that $\phi = 0$ (modulus 2π) on each wall [5]. Assume, for instance, that at time $t = 0$ we have $\phi = 0$ everywhere (Fig. 2, dashed line). At a later time t smaller than L^2/D the angle ϕ has rotated to $\phi = \Omega t$ in a central region, but it drops to zero in a diffusion region of size $(Dt)^{1/2}$ near each wall (Fig. 2, solid line). In these regions we have a

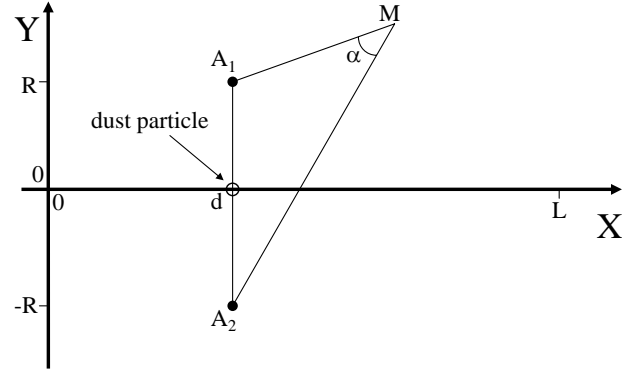


Fig. 3. Nematic monolayer confined between $x = 0$ and $x = L$ under the influence of driven rotations. The dust particle is at $x = d$ and $y = 0$. When elastic stresses are too large, two point disclinations at A_1 and A_2 appear.

strong gradient

$$\frac{\partial\phi}{\partial x} = c \frac{\Omega t}{(Dt)^{1/2}} = c\Omega \left(\frac{t}{D}\right)^{1/2}, \quad (7)$$

where the constant above, $c = 2/\sqrt{\pi}$, is taken to be unity in subsequent calculations [6].

When this gradient reaches some critical value κ , a “burst” may occur. But we have to be careful: this burst is a nucleation process for a new structure. Nucleation in nature is not controlled by the ideal (homogeneous nucleation) threshold. It is catalysed by a dust particle, a cosmic ray, or some other perturbation. A realistic formulation requires that we put a point-like “dust particle” somewhere in the trough. We assume that a burst will occur when the magnitude of the gradient at this point $|\nabla\phi|$ reaches a critical value κ . At all other points $|\nabla\phi|$ may possibly exceed κ .

Thus, we start our discussion by looking at Figure 3 and imposing that one dust particle is located at some point $x = d$ and $y = 0$. We impose that $d \ll \sqrt{Dt} \ll L$ to be in the region described by equation (7). When the local gradient $\partial\phi/\partial x$ located at the point x reaches the critical value κ , a new scenario must start.

4 The first burst

The first breaking event occurs when $\partial\phi/\partial x$ described by equation (7) reaches the critical value κ . This corresponds to a time $t_1 = \kappa^2 D/\Omega^2$. We think of κ values of order 10^5 cm^{-1} (comparable to the inverse size of the dust particle). Thus, t_1 is of order 1 hour and the corresponding diffusion length is $(Dt_1)^{1/2} \sim 1 \text{ mm}$. Our solution after the burst implies a pair of disclinations A_1 and A_2 located at $x = d$ and $y = \pm R(t)$, see Figure 3. The initial value of R is comparable to the dust particle size. The ϕ field is then described by

$$\phi = x \frac{\partial\phi(t)}{\partial x} + \phi_1 = \phi_0 + \phi_1, \quad (8)$$

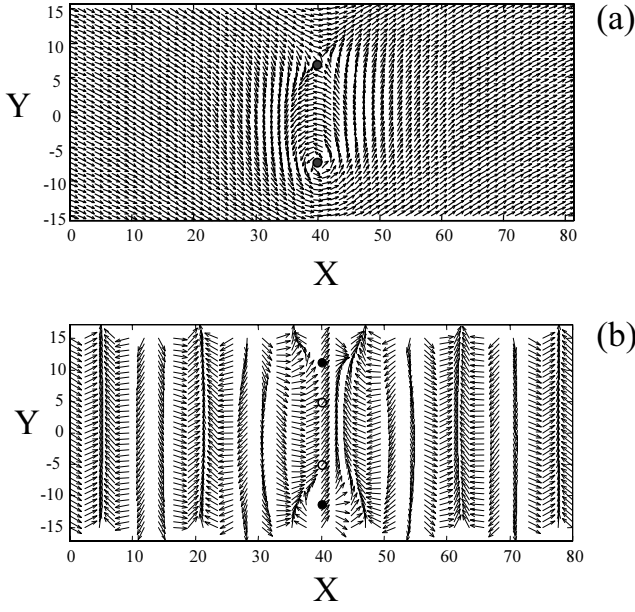


Fig. 4. (a) Ferro-nematic vector in the xy plane from ϕ_1 of the pair disclination of Figure 3. The two point defects are marked with filled circles. (b) Orientation vector corresponding to the field $\phi = \phi_0 + \phi_1$ given by equations (8) and (9). Empty and filled circles mark the initial and final location of the point defects in the simulation, respectively. Lengths are scaled by $a = 10^{-7}$ cm.

where the first term corresponds to equation (7) and ϕ_1 is due to the disclination, and is given simply by

$$\phi_1(M) = \alpha. \quad (9)$$

Here α is the angle $\widehat{A_1 M A_2}$ defined as in Figure 3, and $M \equiv (x, y)$ is the observation point. ϕ_1 satisfies the equation $\nabla^2 \phi_1 = 0$, as first noticed by F.C. Frank (see Fig. 3). We assume that the distance $2R = A_1 A_2$ is small compared to the wall distance, $R \ll d$, and therefore the boundary conditions at the wall are satisfied without including images. Since $\nabla \phi_1$ is opposed in direction to the unperturbed gradient $\nabla \phi_0$, the disclination pair reduces the elastic energy F_{el}

$$F_{el} = \frac{1}{2} K \int (\nabla \phi)^2 dx dy = E_0 + E_1 + E_2, \quad (10)$$

where E_0 is the unperturbed form, while

$$E_1 = \int K \nabla \phi_0 \nabla \phi_1 dx dy \quad (11)$$

can be reduced to a line integral along $A_1 A_2$,

$$E_1 = \int_{A_1}^{A_2} K \nabla \phi_0 [\phi_1] dl = -K |\nabla \phi_0| 4\pi R, \quad (12)$$

where we introduced a cut along the (A_1, A_2) segment, and the discontinuity of ϕ_1 is $[\phi_1] = 2\pi$. Finally, E_2 is the energy of the disclination pair in an undistorted medium

$$E_2 = \frac{1}{2} K \int (\nabla \phi_1)^2 dx dy = 2\pi K \ln \left(\frac{R}{a} \right). \quad (13)$$

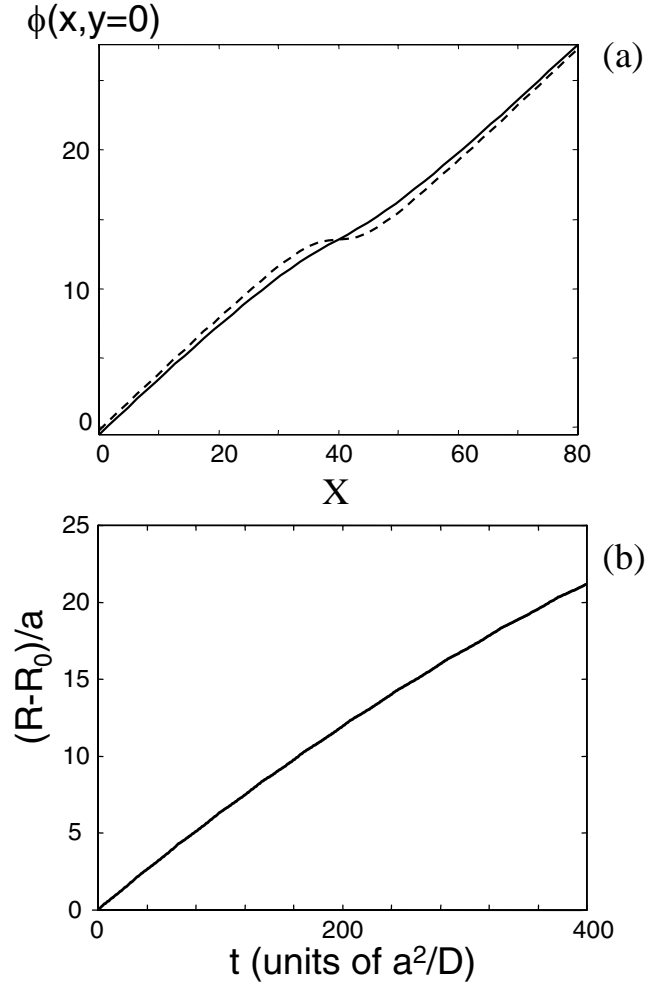


Fig. 5. (a) The dashed line is a plot of ϕ as a function of x just after the first burst. The dust particle is at $x = 40$ (x -axis scaled by $a = 10^{-7}$ cm). The gradient $\phi'(x)$ is reduced near the particle. The solid line shows the profile at some later time. (b) Plot of the defect location $R(t)$ as a function of time. The near-linear behavior is in accord with equations (14) and (15). We used $D = 10^{-6}$ cm²/s and $\kappa = 10^6$ cm⁻¹.

Here a is proportional to the core radius of the disclination.

The force acting on A_1 has an attractive component derived from equation (13) and a repulsive component derived from (12)

$$f_1 = -\frac{1}{2} \frac{\partial}{\partial R} (E_1 + E_2) = 2\pi K \left(|\nabla \phi_0| - \frac{1}{2R} \right). \quad (14)$$

At the moment of burst $|\nabla \phi_0|$ has its threshold value κ . The regime of interest is $R \gg \kappa^{-1}$, and the force is simply $f_1 = 2\pi\kappa K$. As is known for nematics [3], a disclination line moving in a constant force has a (nearly) constant velocity v

$$v = \dot{R} = f_1 / \zeta, \quad (15)$$

where ζ is a friction coefficient due to the rotations induced by the moving line

$$\zeta = \pi\gamma_1 \ln\left(\frac{L}{a}\right). \quad (16)$$

We conducted a numerical study where $\partial\phi/\partial t = D\nabla^2\phi$ was solved with different but convenient boundary conditions, namely $\phi = 0$ at the left wall and $\phi = \Omega t$ at the right wall. The dust particle was assumed to be half-way between the walls. Figure 4(b) shows the director in the xy plane at some time after the first burst, *i.e.* after a disclination pair is created. It consists of a sum of the uniformly changing field ϕ_0 and the disclination given by ϕ_1 . Filled circles mark the defect cores while empty circles mark the cores just after the burst.

Figure 5(a) is a plot of ϕ as a function of the lateral coordinate x , for $y = 0$ in Figure 4(b). The solid line corresponds to Figure 4(b) while the dashed line is just after the burst event. Clearly, the gradient $\phi'(x)$ is lowered near the dust particle ($x = 40$). In Figure 5(b) we show the time evolution of the inter-pair distance $R(t)$. In the simulation we have $R\kappa \gg 1$ and the nearly linear dependence of R on t is evident.

5 The sequence of bursts

We return now to the original problem, with an unperturbed gradient described by equation (7). It is easy to see that just after the first burst at $t = t_1 = \kappa^2 D/\Omega^2$ (and ignoring a factor of $1/c^2 \simeq 0.8$ in Eq. (7)), the correction to the gradient near the dust particle is $\partial\phi_1/\partial x = -2/R$, so that the gradient of ϕ in the x -direction is reduced. After the burst, ϕ increases with time. The second burst appears when the gradient becomes again equal to κ ,

$$\kappa = \frac{\Omega t_2}{(Dt_2)^{1/2}} - \frac{2}{R} \frac{1}{t_2 - t_1}. \quad (17)$$

We introduce the notation

$$\theta_n = (\Omega t_n)^{1/2}, \quad (18)$$

$$\lambda = (D/\Omega)^{1/2}. \quad (19)$$

With this notation we find that $\theta_1 = \kappa\lambda \simeq 10^2$ is a rather large number. Using $R = \dot{R}t = D\kappa t$ and $\Omega\lambda/D\kappa = 1/\kappa\lambda$, equation (17) can be rewritten in the form

$$\theta_2 = \kappa\lambda + \frac{1}{\kappa\lambda(\theta_2^2 - \theta_1^2)}. \quad (20)$$

Analysis of this equations reveals that θ_2 is rather close to θ_1 : treating $\kappa\lambda$ as a large number one can obtain that

$$\theta_2 \simeq \kappa\lambda + \frac{1}{\sqrt{2}\kappa\lambda}. \quad (21)$$

The second term on the right-hand side is very small compared to the first one. What is the time difference between the first and second bursts? If $\Omega = 1 \text{ s}^{-1}$ then

$t_2 - t_1 = 1.4 \text{ s}$. Thus, the bursts start to be frequent once we wait more than the long time t_1 .

Using the assumption $\kappa \gg 1/R$ (meaning that the defects ϕ_1 interact mainly with ϕ_0 but not with themselves), we get for the n -th burst event

$$\kappa = \frac{\Omega t_n}{(Dt_n)^{1/2}} - \frac{2}{R} \left(\frac{1}{t_n - t_{n-1}} + \frac{1}{t_n - t_{n-2}} + \dots + \frac{1}{t_n - t_1} \right). \quad (22)$$

Or, written differently,

$$\theta_n = \kappa\lambda + \frac{1}{\kappa\lambda} \sum_1^{n-1} \frac{1}{\theta_n^2 - \theta_m^2} \quad (23)$$

The solution for θ_2 obtained above (Eq. (21)) suggests that the sequence of bursts has the form $\theta_n = \kappa\lambda + An^\alpha$, with $\kappa\lambda \gg An^\alpha$. We put this form of θ_n and approximate the sum by an integral,

$$An^\alpha \simeq \frac{1}{\kappa\lambda} \int_1^{n-1} \frac{1}{2A\kappa\lambda} \frac{dm}{n^\alpha - m^\alpha}. \quad (24)$$

We change the variable from m to $p = m/n$:

$$An^\alpha = \frac{n}{2A(\kappa\lambda)^2 n^\alpha} \int_{1/n}^{1-1/n} \frac{dp}{1 - p^\alpha}. \quad (25)$$

This equation is satisfied if $\alpha = 1/2$. In this case the integral on the right-hand side is equal to $\frac{1}{2} \ln(n-1) + \frac{1}{2} \ln((2n+1)/(n+1))$, and can be approximated by unity because of the logarithmic dependence on n . In this approximation, we find that $A = \frac{1}{\sqrt{2}} \frac{1}{\kappa\lambda}$. In summary, the burst sequence is given by

$$\theta_n = \kappa\lambda + \frac{1}{\sqrt{2}} \frac{1}{\kappa\lambda} n^{1/2}. \quad (26)$$

The time difference between two successive bursts increases as $n^{1/2}$,

$$t_{n+1} - t_n \simeq \frac{1}{\Omega} \sqrt{\frac{n}{2}} \quad (27)$$

and is of the order of few seconds.

6 Conclusion

We have studied a ferro-nematic monolayer under the influence of water evaporation. This evaporation introduces an external torque tending to rotate the individual molecules. Frustration should occur because the molecules at the edges of the Langmuir trough are anchored to the walls. In the case of non-polar nematics, similar defects will be created (albeit with different symmetry), and we expect only a change in numerical factors in Section 5.

For a simple geometry, we show that a dust particle or some other disturbance can initiate a pair of disclinations, thus relieving the stress near the particle. The distance between the two disclination points increases linearly with time, until the local strains near the particle again reach their threshold. At this time two more disclinations are born, also moving away from each other, and the process continues.

What would happen in a more realistic geometry, for instance with a circular trough, and anchoring condition which imposes a director normal to the walls? In this case, the ideal starting configuration at $t = 0$ would have a disclination point at the center of the trough. When we switch on the evaporation process at $t = 0$, the alignment around this point would rotate uniformly in time: $\phi(x, y, t) = \phi(x, y, 0) + \Omega t$. But near the walls, in a zone of width $(Dt)^{1/2}$, we would find strong gradients, and dust particles could initiate certain “ladders of bursts”.

There are few practical complications to be expected:

- a) The initial state will usually involve many disclination points rather than one. We still expect a uniform rotation of the pattern in the central region —this probably corresponds to the experiment of reference [1]. One could remove the disclination from the central region by preparing the sample under a horizontal magnetic field H , and then switching off the field at $t = 0$.
- b) Our description of the nemato-hydrodynamics was simplistic [3]. With a fuller description we might expect certain backflow effects —the dust particles might move in the xy plane.
- c) The width $(Dt_1)^{1/2}$ of the diffusion layer (at the onset of the ladders) is expected to be rather small, about a millimeter. In this region, the monolayer need not be flat, as a meniscus will be created near the walls.

A final remark: there is a superficial analogy between rotations due to evaporation, which we discuss here, and the rotations induced in a nematic by a rotating magnetic field [3]. But there is a deep difference. When the field is present, the rotational symmetry is broken, and the defects generated by frustration are *domain walls*. But in our case, rotational symmetry is preserved and the relevant defects are *disclination lines*.

Appendix A. Burst sequence in one dimension

We now discuss the series of burst events in the one-dimensional case, namely ϕ depends on one variable only, x . The time t_1 where the first event occurs is given by

$$\kappa = \frac{\Omega t_1}{(Dt_1)^{1/2}}. \quad (\text{A.1})$$

In our prescription, the defect is created in a “delta-function” manner, *i.e.* one molecule changes its orientation. After some time, this single molecule affects its neighborhood in a diffusive manner. Hence,

we write that the slope is reduced by a value $\sqrt{\pi/D(t-t_1)} \exp\left(-\frac{(x-d)^2}{\sqrt{2D(t-t_1)}}\right)$, where d is the particle location. At the second burst event, the total slope $\phi'(d)$ is again equal to the threshold value κ , and hence we have at t_2

$$\kappa = \frac{\Omega t_2}{(Dt_2)^{1/2}} - \frac{\sqrt{\pi}}{\sqrt{D(t_2-t_1)}}. \quad (\text{A.2})$$

Similarly, the n -th event is given by

$$\kappa = \frac{\Omega t_n}{(Dt_n)^{1/2}} - \sqrt{\frac{\pi}{D}} \left(\frac{1}{\sqrt{t_n-t_1}} + \frac{1}{\sqrt{t_n-t_2}} + \dots + \frac{1}{\sqrt{t_n-t_{n-1}}} \right). \quad (\text{A.3})$$

Using $\theta_n = (\Omega t_n)^{1/2}$ and $\lambda = (D/\Omega)^{1/2}$, we rewrite the last equation as

$$\theta_n = \lambda \kappa + \pi^{1/2} \sum_1^{n-1} \frac{1}{\sqrt{\theta_n^2 - \theta_m^2}}. \quad (\text{A.4})$$

We continue to solve this relation assuming that $\theta_n = An^\alpha + \lambda\kappa$, and that on the right-hand side of equation (A.4), $\lambda\kappa$ is larger than the sum. We also approximate the sum by an integral, and find that

$$An^\alpha = \frac{\pi^{1/2}}{\sqrt{2\lambda\kappa An^\alpha}} \int_0^n \frac{dm}{\sqrt{1 - \left(\frac{m}{n}\right)^\alpha}}. \quad (\text{A.5})$$

This equation is satisfied when $\alpha = 2/3$: in this case the variable in the integral can be changed from m to $p = nm$, and the integral becomes equal to $3\pi/4$. In summary,

$$\begin{aligned} \theta_n &= An^\alpha + \lambda\kappa, \\ n &= 2/3, \\ A &= \frac{1}{8}\pi \left(\frac{3}{4}\right)^{3/2} \frac{1}{(\lambda\kappa)^3}. \end{aligned} \quad (\text{A.6})$$

The above sequence of events could be relevant for a one-dimensional superconductor rod. If the rod is thin, in each cross-section the phase is constant. When a current is driven into the system, this phase changes continuously along the rod. When the phase gradient is too large, a similar defect should be created, nucleating most probably around a mechanical “weak spot”. The detailed nucleation process was discussed long ago by Langer and Ambegaokar [7].

References

1. Y. Tabe, H. Yokoyama, *Nat. Mater.* **2**, 806 (2003).
2. For convenience, we define $\Delta\mu$ for unit mass of the water rather than per water molecule.
3. P.-G. de Gennes, J. Prost, *The Physics of Liquid Crystals*, second edition (Oxford University Press, 1995).

4. Note that our anchoring energy depends on the cosine and not on cosine squared, because we are dealing with a ferromagnetic.
5. The periodicity is 2π because we deal with a ferromagnetic where $\phi = 0$ and $\phi = \pi$ are not equivalent.
6. One can obtain the solution to equation (4) with boundary conditions $\phi(x = 0) = 0$ and $\phi(x = \infty) = \Omega t$, by taking $z(x, t) = \Omega - \partial\phi(x, t)/\partial t$. It then follows that $z = \Omega[1 - \text{Erf}(\frac{1}{2}x/\sqrt{Dt})]$. At the origin we thus find that $\partial\phi(0)/\partial x = \frac{2}{\sqrt{\pi}}\Omega (\frac{t}{D})^{1/2}$.
7. J.S. Langer, V. Ambegaokar, Phys. Rev. **164**, 498 (1967).