

Electronic supplementary information (ESI)

for

“Local Distortion Energy and Coarse-Grained Elasticity of the Twist-Bend Nematic Phase”

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1. Local Distortion Energy in the Elastic-Instability Model

The basic idea of the elastic-instability model ¹ is that the bent shape of the highly anisotropic mesogenic molecules reduces the K_{33} elastic constant, making the bend less costly. This effect can be understood as a bend torque applied by the nematic molecule on its neighbors and, on average, on the director \mathbf{n} . If this torque becomes very strong, K_{33} may change sign, transforming the uniform state $\nabla\mathbf{n}=0$ into a local maximum or saddle point of the elastic energy: the nematic is spontaneously bent to avoid this *unstable equilibrium* state, which gives rise to elastic instabilities.

This counter-intuitive $K_{33}<0$ picture raised strong objections. However, recent experimental ²⁻⁴ and theoretical ⁵⁻⁷ studies confirm it, e.g. showing strong pretransitional decrease of K_{33} for bent-shape nematogens. To understand the physical meaning of $K_{33}<0$, let us consider the Landau – de Gennes expansion of the nematic energy $f_{LdG}(\mathbf{Q}, \nabla\mathbf{Q}, \nabla\nabla\mathbf{Q}, \dots)$ in series of the order parameter tensor \mathbf{Q} and its gradients. For constant scalar order parameter S , one-dimensional variation of the director $\mathbf{n}=\mathbf{n}(z)$ and up to fourth order in the gradient operator, it transforms ¹ into a *minor extension* of Frank’s ⁸ curvature energy:

$$f(\mathbf{n}, \nabla\mathbf{n}, \nabla\nabla\mathbf{n}, \dots) = \frac{1}{2} [K_{11}\mathbf{s}^2 + K_{22}t^2 + K_{33}\mathbf{b}^2] + \frac{1}{4} \left\{ C_1 \left[\frac{d^2(n_i n_k)}{dz^2} \right]^2 + 2C_2 \left[\frac{d^2(n_z n_k)}{dz^2} \right]^2 + C_3 \left[\frac{d^2(n_z^2)}{dz^2} \right]^2 \right\}, \quad (\text{S1})$$

containing all the terms allowed by the uniaxial nematic symmetry (for achiral molecules). Here, the vectors $\mathbf{s} = \mathbf{n}(\nabla \cdot \mathbf{n})$ and $\mathbf{b} = \mathbf{n} \times (\nabla \times \mathbf{n})$, and the pseudo-scalar $t = \mathbf{n} \cdot (\nabla \times \mathbf{n})$ describe respectively the splay, bend and twist distortion of the director, and C_i are fourth-order elastic coefficients. The sign of all the *second-order* coefficients in the energy density (S1), including K_{33} , may be *positive or negative*, as long as the positive fourth order terms bound from below the density energy. In fact, the usual $K_{ii} > 0$ condition holds only if the series is cut-off at the second order terms, and is not imposed by any physically-sound selection rules, e.g. based on symmetry.

For $K_{33} > 0$, the solution minimizing eqn (S1) is the usual uniform nematic. For $K_{33} < 0$, two different spontaneously distorted solutions are possible ¹, the twist-bend and splay-bend solutions (the pure bend is geometrically forbidden). In the twist-bend case, of interest here, the director field is heliconical, $\mathbf{n}(z) = (\sin \theta \cos qz, \sin \theta \sin qz, \cos \theta)$. For a perfect heliconical structure, the energy reduces, in the $\sin^2 \theta \ll 1$ limit, to

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$$f_{ib} = \frac{1}{2} \left[K_{22} q^2 \sin^4 \theta + K_{33} q^2 \sin^2 \theta \cos^2 \theta + C q^4 \sin^2 \theta \right] \simeq \frac{1}{2} \left[K_{22} q^2 \sin^4 \theta + K_{33} q^2 \sin^2 \theta + C q^4 \sin^2 \theta \right], \quad (\text{S2})$$

with $C=C_1+C_2$ (here, we anticipate the result of eqn (S3), showing that for small values of $|K_{33}|$, both $\sin^2 \theta_0$ and q_0^2 are small and proportional to $|K_{33}|$. We then only keep the terms up to order $|K_{33}|^3$, which simplifies substantially the calculations). For $K_{33} > 0$, the energy is minimized for $\theta = 0$, the usual uniform nematic, whereas for $K_{33} < 0$ the stable solution is the twist-bend nematic with:

$$\sin^2 \theta_0 = -\frac{K_{33}}{3K_{22}}; \quad q_0^2 = -\frac{K_{33}}{3C}; \quad f_0 = \frac{1}{6} K_{33} q_0^2 \sin^2 \theta_0 = -\frac{1}{2} K_{22} q_0^2 \sin^4 \theta_0. \quad (\text{S3})$$

A second order N – N_{TB} phase transition is expected at the temperature T* defined by $K_{33}=0$. Both $\sin^2 \theta_0$ and q_0^2 behave as order parameters of this transition¹, resulting in an atypical temperature dependence of the condensation energy f_0 . Assuming, as usual, a linear variation of K_{33} close to T*, $K_{33} = a(T - T^*)$, and neglecting the slow temperature dependence of the other constants, we obtain $f_0 \sim (T - T^*)^3$, instead of the usual $(T - T^*)^2$ dependence.

Close to T*, $|K_{33}| \ll 1$ and we can choose $\sin^2 \theta_0 \ll 1$ as a small parameter for the calculation of the coarse-grained (CG) energy coefficients, keeping systematically only the terms of lower order in $\sin^2 \theta_0$ (and therefore in $|K_{33}|$).

2. Coarse-Grained Approximation

The coarse-grained energy

$$f_{TB}^{CG} = f_{TB}^{cond}(|\sigma|) + f_{TB}^{grad}(\sigma, \delta \mathbf{N}) + f_{TB}^{dist}(\nabla \delta \mathbf{N}), \quad (\text{S4})$$

where $f_{TB}^{grad}(\sigma, \delta \mathbf{N}) = \gamma_{\parallel} |\nabla_{\parallel} \sigma|^2 + \gamma_{\perp} |(\nabla_{\perp} - i q_0 \delta \mathbf{N}) \sigma|^2$

$$\text{and } f_{TB}^{dist}(\nabla \delta \mathbf{N}) = \frac{1}{2} \left[K_{11}^N (\mathbf{s}^N)^2 + K_{22}^N ((t^N)^2 - 2 t_0^N t^N) + K_{33}^N (\mathbf{b}^N)^2 \right]$$

is based on the uniaxial large-scale symmetry of the N_{TB} phase. As long as the deviations $\delta \sigma$ and $\delta \mathbf{N}$ from the equilibrium values remain small and with slow spatial variations, this expression is valid and independent of the choice of the local elasticity model.

To calculate the coefficients in eqn (S4) we use explicitly the elastic-instability model¹. We only consider small deviations from equilibrium and we average the energy density over one period of the undistorted twist-bend nematic. Obviously, this procedure only makes sense if the results, in terms of the amplitude, δ , and relaxation length, λ , of the distortions, are compatible with the CG approximations, $\delta^2 \ll 1$ and $\lambda^2 q_0^2 \gg 1$. Coarse-grained results violating these conditions are clearly unphysical and will be discarded. In such a case, one should apply directly the local elastic model, instead of the coarse-grained approach (for example, this is probably the case when edge dislocations of the N_{TB} pseudo-layers are considered).

We note that the distortion energy may be transformed into the more usual expression

$$f_{TB}^{dist}(\nabla \delta \mathbf{N}) = \frac{1}{2} \left[K_{11}^N (\mathbf{s}^N)^2 + K_{22}^N (t^N - t_0^N)^2 + K_{33}^N (\mathbf{b}^N)^2 \right] + const ,$$

often used in similar contexts with omission of the constant term $-K_{22}^N (t_0^N)^2 / 2$. We avoid this approach here, because the “constant” term is strongly temperature-dependent and should be explicitly taken into account, e.g. when comparing the energies of the N and N_{TB} phases.

2.1 Condensation Energy of the Twist-Bend Nematic

The condensation energy of the distorted N_{TB} is obtained directly from eqn (S2) by assuming $|\sigma| = |\sigma_0| + \delta\sigma$, i.e. $\theta \approx \theta_0 + \delta\theta$, and $q = q_0$:

$$f_{TB}^{cond}(|\sigma|) = f_0 + K_{\delta\sigma} \delta\sigma^2 \quad (S5)$$

where $f_0 \approx -K_{22} q_0^2 \theta_0^4 / 2$ is the N_{TB} condensation energy at equilibrium and $K_{\delta\sigma} \approx -2K_{33} q_0^2 / 3$ is an elastic coefficient describing the excess energy due to a small variation $\delta\theta$ of the heliconical tilt angle. Note that we assume here $q = q_0$, as the compression energy is already taken into account in the γ_{\parallel} term of the CG energy.

2.2 Gradient Energy of the Twist-Bend Nematic

The calculation of the coefficient γ_{\parallel} is straightforward, assuming $|\sigma| \equiv |\sigma_0|$, $\delta \mathbf{N} \equiv 0$ and a small uniform variation of the wave vector, $q = q_0 + \delta q$, $\delta q^2 \ll 1$. Comparing the CG expression with the excess local energy, due to the “layer” compression, we obtain:

$$\gamma_{\parallel} = -2K_{33} / 3. \quad (S6)$$

This expression (as well as that for $K_{\delta\sigma}$) has been derived without using the CG approximations, and remains valid even for strong layer compression.

The γ_{\perp} coefficient has been already calculated⁹ (with slightly different notations) by considering a small uniform tilt of the optic axis, $\delta \mathbf{N} \neq 0$, $\delta \mathbf{N}^2 \ll 1$, $|\sigma| \equiv |\sigma_0|$ and $q \equiv q_0$:

$$\gamma_{\perp} = (K_{11} + K_{22}) / 4, \quad (S7)$$

where we averaged over one heliconical period, i.e. this result is really coarse-grained. We note that this value has been used to predict⁹ the CB7CB pitch, $p \approx 7$ nm, in excellent agreement with the experimentally measured value $p \approx 8$ nm^{4, 10}. This successful prediction strongly supports the CG approach and the local elastic model used here.

2.3 Energy for the Distortion of the Optic Axis

To calculate the energy contribution due to the distortion of the optic axis \mathbf{N} , we assume $|\sigma| \equiv |\sigma_0|$, $q \equiv q_0$ and $\delta \mathbf{N} = (0, \alpha(\mathbf{r}), 0)$. Here $\alpha(\mathbf{r})$ is a small tilt of \mathbf{N} , $\alpha^2 = \delta \mathbf{N}^2 \ll 1$, varying

slowly on the scale of the heliconical pitch, $p|\nabla\alpha| \ll 1$. We consider separately the cases of pure twist, splay and bend distortions of \mathbf{N} , assuming that α is a function of only one coordinate, $\alpha = \alpha(x_i)$, with $x_i = x, y, z$ respectively. The director \mathbf{n} rotates on a twist-bend cone which is tilted at angle α with respect to the \mathbf{z} -axis:

$$\mathbf{n}(x_i, z) = \begin{pmatrix} \sin\theta_0 \cos(q_0 z) \\ \cos\alpha(x_i) \sin\theta_0 \sin(q_0 z) + \sin\alpha(x_i) \cos\theta_0 \\ -\sin\alpha(x_i) \sin\theta_0 \sin(q_0 z) + \cos\alpha(x_i) \cos\theta_0 \end{pmatrix}. \quad (\text{S8})$$

We calculate f_{TB}^{dist} by substituting eqn (S8) in eqn (S1), averaging the energy over one N_{TB} period and keeping only the terms of leading order in the small parameters α^2 and θ_0^2 . This straightforward (but rather tedious) procedure gives the elastic energy as a sum of three terms, proportional respectively to α^2 , $d\alpha/dx_i$ and $(d\alpha/dx_i)^2$, which should be compared with the CG expression. In all three cases, the α^2 term reproduces, as expected, the result $\gamma_\perp = (K_{11} + K_{22})/4$. The linear term $d\alpha/dx_i$ vanishes for the splay and bend cases, $x_i = y, z$. This result is also expected: the spontaneous splay $\mathbf{s}^N = \mathbf{N}(\nabla \cdot \mathbf{N})$ and bend $\mathbf{b}^N = \mathbf{N} \times (\nabla \times \mathbf{N})$ vectors are forbidden by the large-scale D_∞ symmetry of the N_{TB} phase (exactly as in the cholesteric phase⁸). Only for pure twist distortion of \mathbf{N} , described by the pseudo-scalar $t^N = \mathbf{N} \cdot (\nabla \times \mathbf{N}) \neq 0$, the linear term survives, showing a spontaneous twist of the optic axis

$$t_0^N = q_0 \theta_0^2. \quad (\text{S9})$$

This important result requires some discussion. The energy is a true scalar, while t^N is a pseudo-scalar. Therefore, t_0^N should be a pseudo-scalar as well (like the spontaneous twist t_0 in the N^* phase). However, in the N^* case, the pseudo-scalar t_0 is symmetry-allowed only because the molecules are chiral. A similar argument is not valid for the N_{TB} phase constituted by achiral molecules. In this latter case, the source of the spontaneous twist is not molecular but structural: it comes from the doubly degenerate chiral heliconical structure. Indeed, above the $N - N_{TB}$ transition, the spontaneous twist in eqn (S9), $t_0^N = t_0$, vanishes (because the chiral source disappears). eqn (S9) predicts a strong temperature dependence of t_0^N , in contrast to the almost constant t_0 in the cholesteric phase. Moreover, t_0^N has the same symmetry as q_0 , which by definition is a pseudo-scalar: in a mirror image the sign of q_0 is inversed, as well as the handedness of the helix.

To avoid ambiguity, we note that $t_0^N \neq 0$ does not imply unconditionally that the optic axis is spontaneously twisted, $t^N \neq 0$, in the N_{TB} ground-state: although $t^N = t_0^N$ minimizes the distortion energy f_{TB}^{dist} , the minimum of the total CG energy f_{TB}^{CG} might be different. This N_{TB} behavior is the same as in the SmA^* phase, confirming the analogy between the two phases.

The comparison of the calculated $(d\alpha/dx_i)^2$ terms with the CG energy gives for the elastic constants related to the curvature of the optic axis \mathbf{N}

$$K_{11}^N = K_{11} ; K_{22}^N = K_{22} ; K_{33}^N = K_{33} + \frac{1}{2}(K_{11} + K_{22})\theta_0^2 = \frac{1}{2}(K_{11} - 5K_{22})\theta_0^2. \quad (\text{S10})$$

The simple result for the splay and twist cases is easy to understand. In these cases, the optic axis \mathbf{N} and the director \mathbf{n} rotate around two orthogonal axes. The two rotations are approximately uncoupled and the contribution of the cross-terms to the energy are negligible for small θ_0^2 and α^2 .

For the same reasons, the contributions of the C -terms to K_{11}^N and K_{22}^N can be neglected.

In the bend geometry, \mathbf{N} and \mathbf{n} rotate around the same axis and the coupled terms cannot be neglected. With the usual ratio $K_{11}/K_{22} \sim 2$, we expect $K_{33}^N \approx K_{33}/2 < 0$, and fourth-order terms in the \mathbf{N} -distortions are needed to make the CG energy converge. Indeed, our CG calculation gives an additional term of the kind:

$$\frac{1}{2}C \left(\frac{d^2\alpha}{dz^2} \right)^2. \quad (\text{S11})$$

For simplicity, we omitted this term in eqn (S4) because the related penetration length is too short (see further), which shows that the CG approximation is unphysical for optic axis \mathbf{N} bending.

3. Penetration Lengths of the Twist-Bend Nematic

Any distortion of the equilibrium \mathbf{N}_{TB} structure relaxes over some characteristic length-scale. The coherence lengths, ξ_{\parallel} and ξ_{\perp} , describe the exponential relaxation of a small perturbation of the heliconical tilt angle, $\delta\theta$, respectively along and perpendicular to the helix axis. These coherence lengths have been calculated and discussed in the main text. A small perturbation of the optic axis, $\delta\mathbf{N}$, will also relax over an anisotropic characteristic length, the penetration length of the \mathbf{N} -distortions.

To estimate the penetration lengths λ_i , $i=1,2,3$, corresponding to the main modes, respectively splay, twist and bend, of distortion of the optic axis \mathbf{N} , we consider again a small tilt $\delta\mathbf{N} = (0, \alpha(\mathbf{r}), 0)$ imposed at the boundary of the sample, e.g. by surface anchoring (Fig. S1). Except for the distortion of \mathbf{N} , we assume a perfect \mathbf{N}_{TB} structure, with $|\sigma| \equiv |\sigma_0|$ and $\mathbf{q} \equiv \mathbf{q}_0$.

For the splay case, the energy due to the tilt of the optic axis is $\gamma_{\perp} q_0^2 \theta_0^2 \alpha^2$, the “gradient” energy is $K_{11}^N (d\alpha/dy)^2/2$, and the total energy is minimized for

$$\alpha(y) = \alpha_s \exp(-y/\lambda_1) \quad ; \quad \lambda_1 = \sqrt{\frac{K_{11}^N}{2\gamma_{\perp} q_0^2 \theta_0^2}} = \frac{1}{q_0 \theta_0} \sqrt{\frac{2K_{11}}{K_{11} + K_{22}}}, \quad (\text{S12})$$

where α_s is the tilt of \mathbf{N} imposed at the surface. A similar result is obtained in the twist case

$$\alpha(x) = \alpha_s \exp(-x/\lambda_2) \quad ; \quad \lambda_2 = \sqrt{\frac{K_{22}^N}{2\gamma_{\perp} q_0^2 \theta_0^2}} = \frac{1}{q_0 \theta_0} \sqrt{\frac{2K_{22}}{K_{11} + K_{22}}}. \quad (\text{S13})$$

In both cases, $\lambda_i \approx 1/q_0 \theta_0 \gg 1/q_0$, satisfying the main coarse-grained condition of slow variation of the tilt on the scale of the heliconical pitch p .

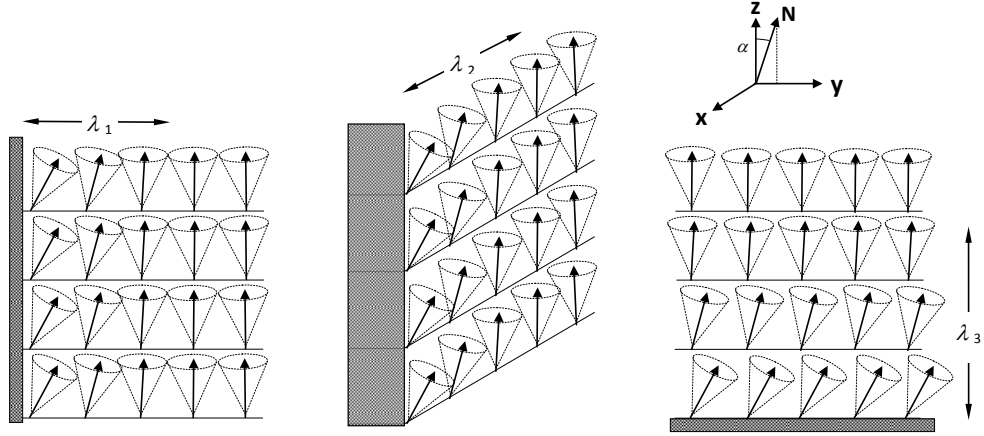


Fig. S1. Penetration lengths λ_i , $i=1,2,3$, for the main distortion modes of the optic axis \mathbf{N} , respectively splay, twist and bend. A small tilt $\delta\mathbf{N}=(0,\alpha(\mathbf{r}),0)$ of the optic axis, imposed on the surface boundary, penetrates in the bulk twist-bend nematic only over the length-scale defined by λ_i .

The bend case is more complicated due to the negative bend constant K_{33}^N . Oscillating solutions are now possible, with splay-bend or twist bend superstructures of the optic axis \mathbf{N} . In both cases, we need to take into account the fourth-order term in eqn (S11), in order to avoid the divergence of the oscillation of wave vector \mathbf{k} . For a splay-bend distortion of \mathbf{N} , the excess CG energy due to $\delta\mathbf{N}=(0,\alpha(z),0)$ reads:

$$\gamma_{\perp} q_0^2 \theta_0^2 \alpha^2 + \frac{1}{2} C \left(\frac{d^2 \alpha}{dz^2} \right)^2 + \frac{1}{2} K_{11}^N \alpha^2 \left(\frac{d\alpha}{dz} \right)^2 + \frac{1}{2} K_{33}^N \left(\frac{d\alpha}{dz} \right)^2. \quad (\text{S14})$$

After linearization, the solution of the Euler – Lagrange equation is a damped oscillation:

$$\alpha \sim \exp(-z/\lambda_3) \sin k_3 z, \quad \text{with } \lambda_3 = \left(q_0 \theta_0 \sqrt{\frac{\gamma_{\perp}}{2C} + \frac{K_{33}^N}{4C}} \right)^{-1/2}; \quad k_3 = \left(q_0 \theta_0 \sqrt{\frac{\gamma_{\perp}}{2C} - \frac{K_{33}^N}{4C}} \right)^{1/2}. \quad (\text{S15})$$

Taking $K_{33}^N \approx K_{33}/2$ as before, we obtain $\lambda_3 \approx 2/q_0$; $k_3 \approx q_0$. These values are incompatible with the approximations used in the calculation of the coefficients of the coarse-grained energy. Similar results are obtained if we consider a twist-bend structure of the optic axis \mathbf{N} .

Therefore, the relaxation of the bend of \mathbf{N} , occurring over a scale smaller than the N_{TB} pitch p , cannot be described in the CG model. In some cases, for example in the vicinity of an edge dislocation, the local elastic model should be used directly, instead of the simpler CG approach.

4. Analogy with the TGB_A phase

By analogy with SmA*, we expect that the Type I / Type II behavior of the NTB phase will depend on the value of the relevant Ginsburg parameter,

$$k_t = \frac{\lambda_2}{\xi_\perp} = \frac{4K_{22}}{K_{11} + K_{22}}.$$

Taking approximately $K_{11}/K_{22} \sim 2$, we have $k_t \approx 4/3$, which is about twice the value $k_t = 1/\sqrt{2}$ required for Type II behavior. We expect then, for strong enough spontaneous chiral field, $h > h_{c1}$, the penetration of the twist of \mathbf{N} in the N_{TB} structure by nucleation of screw dislocations of the pseudo-layers. The value of k_t does not depend on temperature, as in the SmA^* case. However, the spontaneous twist of the N_{TB} optic axis, $t_0^N = q_0 \theta_0^2$, has a strong temperature dependence, in contrast to the temperature-independent spontaneous twist t_0 in the SmA^* . Therefore, the chiral field applied to the N_{TB} phase, $h = K_{22}^N t_0^N = K_{22} q_0 \theta_0^2$, is also strongly temperature-dependent, unlike its SmA^* analog, $K_{22} t_0$.

The rigorous calculation of the critical field h_{c1} for the TGB_{NTB} , the twist-bend nematic analog of the TGB_A phase, is a difficult task because of the moderate value of k_t . However, again by analogy with the SmA^* ¹¹, we can estimate h_{c1} for strongly Type II N_{TB} materials, $k_t \gg 1$. Let us compare, for $T < T^*$, the energy of the N_{TB} and TGB_{NTB} phases. In a perfect N_{TB} , $t^N = 0$ and the energy density is just the condensation energy, $f(N_{TB}) = -K_{22} q_0^2 \theta_0^4 / 2$. In the TGB_{NTB} phase, the energy is $f(TGB_{NTB}) = -K_{22} q_0^2 \theta_0^4 / 2 + f(\text{disl}) + f(\bar{t}^N)$. Here, $f(\text{disl}) > 0$ is the energy of the network of screw dislocations in the grain boundaries (GB). Approximately, $f(\text{disl}) = \mu / (l_b l_d)$, where μ is the energy cost of dislocation per unit length, l_b is the distance between the GBs, and l_d is the distance between the dislocations on the GB. $f(\bar{t}^N)$ is the energy related to the average twist \bar{t}^N , penetrating in the TGB_{NTB} phase, $f(\bar{t}^N)$. Geometrically, $\bar{t}^N = p / (l_b l_d)$, and taking into account that $\bar{t}^N \ll t_0^N$ close to h_{c1} , we obtain $f(\bar{t}^N) = -hp / (l_b l_d)$. Comparing the energy densities of the N_{TB} and TGB_{NTB} phases, we obtain $h_{c1} = \mu / p$. For $k_t \gg 1$, by analogy with the SmA^* ¹¹, the main contribution to μ is due to the distortion of the “layers” around the dislocation:

$$\mu \approx \gamma_\perp q_0^2 \theta_0^2 \frac{p^2}{4\pi} \ln \frac{\lambda_2}{\xi_\perp}; \quad h_{c1} \approx \left(\frac{K_{11} + K_{22}}{8K_{22}} \ln \frac{\lambda_2}{\xi_\perp} \right) K_{22} q_0^2 \theta_0^2 \approx \left(\frac{3}{8} \ln k_t \right) h \quad (S16)$$

Therefore, the lower critical field h_{c1} and the spontaneous chiral field h differ only by a numerical coefficient and have the same temperature dependence. If $(3/8) \ln k_t < 1$, as expected for moderate k_t values, then $h > h_{c1}$ at any temperature $T < T^*$, and the TGB_{NTB} phase *will always be stable* with respect to the N_{TB} phase. This striking result, if confirmed by a more detailed calculation of $f(\text{disl})$, is one more example of the limitations of the $N_{TB} - SmA^*$ analogy when the temperature dependence is involved.

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