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Critical Stripe-Domain Instability of Nematic Elastomers

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Abstract. – We present an experimental and theoretical investigation of the critical formation of stripe domains in monodomain nematic elastomers. Domains with alternating sense of director rotation are formed when the material is stretched perpendicular to the initial director alignment. A wide range of differing samples are shown to have a singular onset to director rotation at a threshold deformation and a second singular point at the end of the stripe domain region. All the data collapses onto a master plot revealing a universal behaviour. We analyse theoretically the threshold properties of the stripe phase. The analysis of free energy yields a first order transition into a fully-coarsened texture without any intermediate state of sinusoidal modulation.

Large monodomain nematic elastomers can be prepared by the two-step crosslinking under strain of liquid crystalline polymer chains [1]. A uniformly aligned nematic phase coexists with and couples to the rubber elasticity of a percolating network of chains. Such a material is optically transparent because, unlike ordinary nematic liquids, the director \( \mathbf{n} \) is anchored to an initial orientation \( \mathbf{n}_0 \) established at crosslinking, not allowing thermal fluctuations to develop and scatter light. The director can be rotated by imposition of elastic strains [2]. For instance, in a sample extended by a ratio \( \lambda \) in a direction perpendicular to \( \mathbf{n}_0 \), the director \( \mathbf{n} \) will rotate by an angle \( \theta \) from 0 to \( \frac{\pi}{2} \) towards the extension axis. This rotation has been reported as an apparently discontinuous jump [3] or continuous, via a system of stripe domains with alternating sense of the rotation \( \theta \) [4].

Here we report the first experimental observation of the singular onset and saturation of director rotation in nematic elastomers undergoing a strain-induced stripe transition. A wide range of differing nematic elastomers exhibit qualitatively the same pattern of the director rotation. We collapse all the data onto a single master curve given by a model we discuss, thereby demonstrating the universality of outwardly different materials within this picture. Secondly, we theoretically analyse the critical behaviour at the onset of stripes. There is a first order transition to an already coarsened stripe structure, missing completely the linear regime of sinusoidal modulation of the director.

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Fig. 1. — A scheme of stretching experiment. Strain $\lambda$ is along the $\hat{z}$ axis of the sample, perpendicular to the initial director $\mathbf{n}_0$. Solid lines indicate the director orientation in consecutive stripes. Horizontal dashed lines show the domain walls. The director angle $\theta$ and the associated shear $\lambda_{zz}$ decay rapidly near the clamped sample ends.

1. Experimental

Monodomain nematic elastomers were synthesized in a two-step crosslinking reaction as described in [1, 4, 5]. The liquid crystalline monomer (benzoic acid phenyl ester derivative with C$_4$ spacer and methoxy-group in $p$-position) and two crosslinking components were added to poly[oxy(methyl)silylene] with a degree of polymerisation $P_n = 60$. The chemical structures of the components are given in [5]. The elastomers were crosslinked once, then stretched to achieve a macroscopic uniform director orientation of the nematic phase, and crosslinked the second time to lock-in the anisotropic aligned structure of the network.

Nematic elastomers were formed with different crosslink densities, using 5, 7.5, 10, 12.5 and 15 mol% of crosslinking components with respect to the reactive Si-H groups. We refer to these samples by this % figure. The remaining Si-H groups were substituted with the nematic mesogen, thereby forming a standard side-chain liquid crystalline polymer chain. All nematic elastomers show a glass transition temperature $T_g \approx 276$ K and a nematic to isotropic transformation at $T_{ni} \approx 355$ K. The mechanical experiments were performed deep in the nematic phase, at $T = 308$ K, which corresponds to a reduced temperature $T/T_{ni} \approx 0.87$ with only a slight variation for different samples. Further, a different nematic elastomer was synthesized, which has incipient smectic A ordering and possible smectic clusters. This material contained 7.5 mol% of crosslinking components, 55 mol% of nematic mesogens of the previous series and 30 mol% of mesogenic units known to generate only the smectic A phase when polymerised (cyano-group instead of methoxy-group in $p$-position). This sample, referred to as S, has the clearing temperature $T_{ni} = 368$ K, and the experiments were performed at $T/T_{ni} \approx 0.84$.

In order to investigate the director reorientation, thin ($\leq 0.5$ mm) films of elastomers were cut to rectangles $L_x \times L$ of approximately $7 \times 10$ mm, with the uniform director $\mathbf{n}_0$ along the shorter rectangle side. The ends of the sample were clamped as shown in Figure 1. The samples were then deformed in the direction perpendicular to $\mathbf{n}_0$, taking care that the equilibrium is reached after each step of extension. After each step the rotation angle $\theta$ was determined by X-rays — the Debye-Scherer scattering from parallel rods is peaked perpendicular to the director. These peaks split into two distinct pairs corresponding to director rotation by $\pm \theta$. Polarised microscopy can also monitor the director texture. The stripes are not particularly regular...
Fig. 2.—Bulk director rotation angle $|\theta|$ against strain $\lambda$ for samples 5% (○; threshold strain $\lambda_1 \approx 1.02$), 7.5% (□; $\lambda_1 \approx 1.07$), 10% (○; $\lambda_1 \approx 1.07$), 12.5% ($\Delta$; $\lambda_1 \approx 1.10$) and 15% ($\nabla$; $\lambda_1 \approx 1.16$) and the sample S (●; $\lambda_1 \approx 1.15$). The theoretical curve $\theta_0(\lambda)$ from equation (2) is fitted to the sample 5% for a value of mean backbone chain anisotropy $r \approx 2.3$ (solid line). The error in the angle determination is ±3 deg, increasing to ±5 deg near the singular edges of the transition.

but have a characteristic spacing $d \sim 1-10\ \mu\text{m}$ depending on the level of crosslinking. The systematic study of director rotation against deformation for the full range of angles $\theta = (0, \frac{\pi}{2})$ and of samples with varying crosslinking density shows a most characteristic behaviour (see Fig. 2).

The director remains unrotated until the deformation reaches a threshold value $\lambda_1$ which is dependent on the sample crosslinking level. Past the critical threshold, $\theta(\lambda)$ apparently increases continuously and finally reaches saturation at $|\theta| = \frac{\pi}{2}$, again in a critical fashion (a discontinuity in slope $d\theta/d\lambda$). The director angle varies little across a stripe, switching from $+\theta$ to $-\theta$ across a very narrow wall (of width beyond the present experimental resolution), rather than being, say, a periodic modulation $\theta(x) = \theta_0(\pi x/d)$. Beyond the second singular point, $\lambda = \lambda_2$, the director is aligned along the extension axis, $\theta = \pm\frac{\pi}{2}$. These states are equivalent in a nematic with $\mathbf{n} \equiv -\mathbf{n}$ and the sample is again transparent except for faint narrow lines seen under the microscope, which are topological fossil remains of the original $\theta \to -\theta$ walls [6]. Associated stress-strain measurements [5] show that the regions A (before the transition, $\lambda = \{1, \lambda_1\}$) and C (after the rotation is complete, $\lambda > \lambda_2$) have conventional rubber-elastic moduli $\mu \sim 10^5$ N/m$^2$, while the stripe region B ($\lambda = \{\lambda_1, \lambda_2\}$) has a considerably lower modulus.

2. Analysis of Data

The large threshold deformation $\lambda_1 \sim 1.1$, the variation $\theta(x)$ across stripes, the characteristic size $d$ and the characteristic $\theta(\lambda)$ with two singular edges can be compared with the theoretical model [6]. It is predicted [7-9] that Cosserat solids, such as nematic elastomers with an internal degree of freedom $\mathbf{n}$, should be able to deform without cost of energy (soft deformations). This
is easy to understand for elastomers — the free energy rises when chains of the network are stretched and their number of configurations reduced (rubber elasticity). Nematic chains are anisotropic. prolate or oblate along the local director \( n \), and can rotate their anisotropic distributions of configurations without entropy change and thus at constant free energy. Since molecular and macroscopic shape mirror each other, these rotations lead to macroscopic shape changes that are non-trivial deformations \(^{(1)}\).

If network chains are linked in the field- or stress-oriented nematic state and if there any imperfections away from the ideal Gaussian network, a memory of the initial director axis \( n_0 \) is seemingly locked in. Such a material is then believed \(^{[10]}\) to be qualitatively soft, but still requires a small stress to execute one of these special modes. This has been termed “semi-soft” \(^{[6]}\). The drastic reduction of the rubber modulus in the transition region \( B \) is suggestive of semi-soft response. A problem is that such soft modes involve not only a stretch \( \lambda \) but also an associated shear deformation \( \lambda_{xx} \) and this is apparently forbidden by the sample clamps (Fig. 1).

A suggestion \(^{[4,6]}\) is that although gross shear deformation is forbidden, it could occur in narrow alternating bands of \( \pm \theta, \pm \lambda_{xx} \). A conventional rubber-elastic penalty is paid at the clamped ends where the shear is constrained and also in the walls between stripes. In addition, a Frank nematic energy \( \frac{1}{2} K (d\theta/dx)^2 \) (with \( K \) the Frank constant) is generated in the walls. We shall analyse this below. Any alternative approach neglecting the soft deformation concept would lead to the bulk of the rubber deforming in a conventional manner with an energy scale \( \mu \). Then the nematic penetration depth \( \xi = (K/\mu)^{1/2} \sim 10^{-8} \) m is the characteristic length of the problem and the threshold strain \( \varepsilon_1 = \lambda_1 - 1 \sim \xi/L \sim 10^{-6} \) is unphysically small.

We follow a simple nematic extension of classical rubber elasticity theory \(^{[6,8,10]}\). It is clear that the walls and clamped ends are a minor perturbation and can be neglected in showing \(^{[6]}\) that the threshold is determined by the bulk anchoring of \( n \) to the rubber matrix. Considering the bulk only, an optimal local shear allowing the system to follow a semi-soft trajectory yields an elastic free energy density:

\[
f(\theta) = \frac{1}{2} \mu \left[ f_\lambda(\theta) + \alpha \lambda^2 \sin^2 \theta \right], \tag{1}
\]

where \( \mu \) is the rubber energy scale, the shear modulus in the isotropic phase, and \( f_\lambda(\theta) \) is the ideal soft free energy density:

\[
f_\lambda = \lambda^2 + \left( \frac{1}{r} - 1 \right) \lambda^2 \sin^2 \theta + \frac{2\sqrt{r}}{\lambda \sqrt{r + (1 - r) \sin^2 \theta}}
\]

with \( r \equiv \langle \ell_1/\ell_\perp \rangle \) the mean ratio of chain dimensions parallel and perpendicular to the local director \( n \). For a given deformation \( \lambda \) the optimal rotation angle \( \theta_0(\lambda) \) gives \( f_\lambda(\theta_0) = 3 \), its minimal value, and hence there is no energy cost for soft deformations.

The semi-soft addition to \( f_\lambda(\theta) \) \((i.e., \)) the bulk anchoring of the director) can be shown to always have the form \( \alpha \lambda^2 \sin^2 \theta \), with the value of the parameter \( \alpha \) dependent on the physical origins of the bulk director locking in a given material. There are various such mechanisms possible (see a discussion in \(^{[10]}\), for example), which violate the symmetry conditions needed for the Golubovic-Lubensky theorem \(^{[7]}\) to hold. Here we are concerned to only demonstrate the experimental universality of the nematic rubber response and do not discuss a particular mechanism. The optimal director rotation angle \( \theta_0(\lambda) \), obtained by minimising the semi-soft

\(^{(1)}\) We note in passing that the same concept of rotating anisotropic chains at low cost could be invoked to explain extreme shear thinning, the stress instability and shear banding in flowing polymers.
elastic energy (1), is

\[ \theta_0 = \pm \arcsin \left[ \frac{r}{r-1} \left( 1 - \frac{\lambda_1^2}{\lambda_2^2} \right) \right]^{1/2} \] (2)

Non-zero solutions \( \theta_0(\lambda) \) first appear at a \( \lambda_1 \), a threshold determined by the constant \( \alpha \):

\[ \lambda_1 = \left( \frac{r-1}{r-\alpha r-1} \right)^{1/3} \] (3)

The end of transition region B is at \( \lambda_2 = r^{1/2} \lambda_1 \), where \( \theta_0 = \pm \pi/2 \) and cannot change any further.

The ratio of chain step lengths \( r \) can be determined directly from two independent experiments.

(i) When the material is close to being soft, equation (1) dictates that \( r \) is close to the cube of the sample spontaneous deformation, \( \lambda_m \), on cooling to the nematic state. (The relative difference between \( r \) and \( \lambda_m^3 \) must be of the same order as the threshold strain \( \lambda_1 - 1 \), because both are determined by the same physics of semi-softness). In our experiments we have \( \lambda_m^3 \approx 3 \).

(ii) The ratio of the upper and lower phase boundaries is \( \lambda_2/\lambda_1 = r^{1/2} \) (one then extracts \( r \approx 2.6 \) from Fig. 2). We shall focus on parameters \( \lambda_1 \) and \( r \), derived from \( \lambda_2/\lambda_1 \), rather than \( \alpha \), noting that the constraint \( \lambda_2/\lambda_1 \approx \lambda_m^{3/2} \) is closely followed in our experiments.

In Figure 2 we plot the director rotation angle \( \theta(\lambda) \) for nematic side-chain elastomers of crosslink densities varying from 5% to 15% and for a smectogenic copolymer network S. All samples have different thresholds \( \lambda_1 \), which increase with crosslinking density. The solid line in Figure 2 is an example fit of the general equation (2) to the data for sample 5%; it clearly displays the singular behaviour at \( \lambda_1 \) and \( \lambda_2 \). Samples 7.5, 10, 12.5 and 15% all have the same mean anisotropy \( r \approx 2.6 \) (determined from the direct curve fit and, for samples that survived until the end of the stripe regime, independently from the ratio \( r = (\lambda_2/\lambda_1)^2 \)). Samples 5% and S have slightly lower mean backbone chain anisotropy, \( r \approx 2.3 \) and 2.33, respectively. There

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Fig. 3. — All the data for \( \theta(\lambda) \) from the Figure 2 collapsed according to equation (4). Same notations for data points as in Figure 2; the solid line is a curve \([1 - (\lambda_1/\lambda)^2]\).
are microscopic reasons for this reduction: in smectic regions of the system the backbone chain is constrained between the layers in an oblate shape, while with very few crosslinking units (sample 5%) many chains are left dangling free, "diluting" the network — in both cases the average prolate backbone anisotropy $r$ is slightly reduced.

Figure 3 shows the data from all these samples collapsing on a universal curve. by using $\lambda/\lambda_1$ as a relative deformation and rearranging (2) to

$$\frac{r - 1}{r} \sin^2 \theta_0 = 1 - \left(\frac{\lambda_1}{\lambda}\right)^2$$

(4)

This scheme illustrates that the general result (2) accommodates not only varying thresholds, $\lambda_1$ (expressing thermo-mechanical history), but also varying chemical compositions defining the backbone anisotropy $r$. The data follows the universal curve until $\theta_0 = \frac{\pi}{2}$ at which point it saturates to the value $(r - 1)/r$, a constant that may vary from sample to sample depending on their composition. This analysis, and equations (2-4), could also incorporate the observations of an apparently discontinuous jump of $\theta$ from 0 to 90° [3]: for a very small backbone anisotropy $(r - 1)/r \ll 1$ (indeed the case of [3]), the region of stripe domains becomes too narrow to be distinguished.

3. Coarsening of the Transition

The critical region around the threshold $\lambda = \lambda_1$ requires a delicate analysis. Adding the Frank energy to the nematic rubber elastic energy (1) and changing to a dimensionless length $u = x/\xi$ reduced by the nematic penetration depth $\xi = (K/\mu)^{1/2}$, the total free energy takes the form

$$F = A \gamma \int_0^L du \left[ \frac{1}{2} \theta'^2 - \frac{1}{2} p \theta'^2 + \frac{1}{4} q \theta^4 + \ldots \right]$$

(5)

where $\gamma = \sqrt{\mu K}$ is an interfacial energy scale, $A$ is the area $LL_y$ of a domain wall, $L = L_x/\xi$ is the reduced width of the sample across the stripe domains and $\theta' = d\theta/du$. We have expanded the free energy density (5) for small $\theta$ as is appropriate for the critical regime $\lambda \sim \lambda_1$. The coefficients of this Landau expansion are $p = \left(\frac{r - 1}{r}\right) \frac{1}{2} \left[\left(\lambda/\lambda_1\right)^3 - 1\right]$, vanishing at $\lambda = \lambda_1$, and $q = \frac{3}{2\lambda_1} \left(\frac{r - 1}{r}\right)^2 - \frac{1}{2} \frac{r - 1}{r} p$, so that $q \approx \frac{3}{2\lambda_1} \left(\frac{r - 1}{r}\right)^2$ near the transition $\lambda = \lambda_1$. Equation (5) represents a classical energy of an interface between states with $\theta_0 = \pm \sqrt{p/q}$, which are the two values of $\theta$ minimising $F$.

Denoting the relative amplitude of the rotation angle $\eta = \theta_m/\theta_0$, the stripe free energy reduces as $\eta$ increases from 0 to 1, but at the expense of lengthening the period of modulation. The modulation is in general elliptic. There is the usual relation between amplitude and period for this non-linear problem which we now explore in the current context.

Consider the bulk free energy with modulation $\theta(x) = \theta_m \Phi(x)$ characterized by an amplitude $\theta_m$, in general smaller than the optimal semi-soft rotation angle $\theta_0$. For very small $\theta_m < \theta_0$ the period is a constant, $d = 2\pi\xi/\sqrt{p}$, which is the simple pendulum limit of (5): $\theta(x) = \theta_m \sin(2\pi x/d)$, a sinusoidal modulation. In this harmonic limit one ignores the $\theta^4$ term in (5) and finds that $F = 0$. The free energy can be reduced by allowing the amplitude of the rotation angle to increase towards its optimal value $\theta_0$, with $\eta = \theta_m/\theta_0$ serving as an order parameter of this problem. At a fixed $\eta$ and hence the period $d(\eta)$, the director modulation [obtained from the Euler-Lagrange minimization of (5)] is $\theta = \theta_m \text{sn} \left[ \sqrt{p \left(\frac{2 - \eta^2}{2 - \eta^2}\right)} (x/\xi) \right]$ with the period $d(\eta) = (\xi/\sqrt{p}) \left(\frac{2 - \eta^2}{2 - \eta^2}\right)^{1/2} 4K[k^2]$, where $\text{sn}$ and $K$ are an elliptic function and
a complete elliptic integral of modulus \( k^2 = \eta^2/(2 - \eta^2) \). This is explicitly derived in the Appendix.

The profile of the domain wall coarsens to \( \theta(x) = \theta_0 \tanh \left[ \sqrt{p/2}(x/\xi) \right] \) if the system is large enough to allow a transition between the optimal equilibrium values \( \pm \theta_0 \) in the consecutive domains. This would mean that the wall thickness \( \xi \sqrt{2/p} \) is small compared with any imposed domain size \( d \) and represents a coarsened regime where \( \theta \approx \pm \theta_0 \) does not vary appreciably across each stripe domain. Stripes are well-separated and defined.

We have seen that the total bulk free energy decreases as the domain size \( d \) increases, because more of the sample is capable of approaching the optimal value of the director rotation angle \( \theta_0 \). Less of the sample finds itself in an interfacial region of higher energy if stripes are coarsened. However, there is another contribution that works against this tendency to large amplitude and long period — the rubber-elastic energy in the region near clamped sample ends, where the shear deformation associated with the director rotation must be suppressed (see Fig. 1). Where the shear is suppressed, the deformation is no longer semi-soft and hence there is an energy penalty in this volume associated with the clamps. It is possible to show [6] that the distance at which the (periodic) shear in each stripe decays near the clamp is \( \sim d \). In this volume one effectively has to apply a non-soft shear \( \sim \lambda_{zz}(\theta) \) to conform to the clamp, and hence an estimate of the end-energy is \( \mu d \xi L_y \left( \frac{\xi}{\sqrt{\xi}} \right)^2 \int_0^\xi du \theta^2(u) \) (putting in the linear relation between the shear and angle of director rotation). The end-energy rises as \( d \) increases and we must optimize the sum of it and and the bulk energy (5) to determine the period \( d \). Since the end-energy scales as \( L_x L_y \) and the bulk energy as the volume \( V = L_x L_y L \), then a factor of the sample length \( L \) connects them and will enter the critical description.

The calculation of total free energy, \( F_{\text{tot}} \), requires the substitution of elliptic functions for \( \theta(u) \) and subsequent integration over the domain period. The procedure can be carried out analytically and is outlined in the Appendix. Here we graphically present the variation of this free energy, as function of the order parameter \( \eta \), for several characteristic values of strain. The control parameter \( p \) vanishes at the bulk threshold \( \lambda = \lambda_1 \). The plots in Figure 4 clearly indicate that the critical onset of stripe domains proceeds via the first order transition at \( p^* \approx 4.1 p_c \approx 10.3 \times 10^{-3} \left( \frac{\xi}{\xi} \right)^{2/3} \left( \frac{\xi}{\sqrt{\xi}} \right)^{4/3} \) to a value \( \eta \approx 0.9 \). The relative amplitude of the director rotation angle is large, \( \theta_m \approx \theta_0 \), and one is away from the simple pendulum (linear) limit when the transition takes place. However, the modulus \( k^2 \) at the transition is \( k^2 = 0.7 \) and the modulation \( \tanh(\theta) \) may not appear sufficiently coarsened, in comparison with the limiting form \( \sin(\theta) \). In Appendix, in Figure 6, we follow the evolution of the order parameter \( \eta \) and the modulus \( k^2 \) with the increasing strain, represented by the parameter \( (p/p_c) \) in \( F_{\text{tot}}(\eta) \). By \( (p/p_c) \) \( \sim 10 \) the elliptic modulus \( k^2 \) is very close to unity and the fully-coarsened limit, with \( \theta \approx \theta_0 \tanh \left[ \sqrt{p/2}(x/\xi) \right] \) across the domain wall, has effectively been reached. Experimentally the strains \( p \sim p_c \) away from \( \lambda_1 \) are extremely small. For characteristic values \( K \approx 10^{-11} \text{ J/m} \) and \( \mu \approx 10^3 \text{ J/m}^3 \) we have \( \xi \approx 10^{-8} \text{m} \) and then for samples with \( L \approx 1 \text{ cm} \) and backbone chain anisotropy \( r \approx 1.5 \) one obtains \( p_c \approx 10^{-4} \). Thus \( p_c \) is not practically measurable and \( p \approx 10 p_c \) is still a very small relative strain. For all practical purposes systems will be taken through the transition directly to states of high \( k^2 \) and thus of fully coarsened stripes.

The first order character of the transition means also the director discontinuously jumps at the transition to the angle \( \theta_m \approx 0.9 \sqrt{p/q} \). Again it is instructive to put in numbers: at the transition \( p^* = 4.1 p_c \approx 4 \times 10^{-4} \) and \( q \approx 3.3 \frac{3}{2} \lambda_1 \left( \frac{\xi}{\sqrt{\xi}} \right) \approx 1/6 \), which yields a jump of only \( \theta_m \approx 3^\circ \). The underlying singular edge at the threshold [see Fig. 2 and Eq. (2)] means that one could not distinguish between the first and second order pictures by examining the experimental data for \( \theta(\lambda) \) jumps and it is on the coarsening of the stripes that we must rely the interpretation.
4. Summary

We have investigated new transitions to and from the stripe domain state in nematic elastomers under strain and experimentally found singular director variation at each end of the stripe regime. The response of differing samples, although quantitatively distinct, collapses onto a master curve indicating a universality of the underlying physical phenomena. The universal form is given to high precision by a simple nematic extension of classical rubber elasticity. The analysis of this paper suggests that the semi-soft stripe domain phase exists in a wide range of nematic elastomers. A theoretical analysis of the critical onset of stripes shows that a small first order transition intercedes at the $(\lambda - \lambda_1)^{1/2}$ edge, and at the same time generates fully coarsened stripes, rather than a periodic sinusoidal modulation, as is indeed observed.

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Appendix: Reduction to Elliptic Functions of the $-\theta^2 + \theta^4$ Problem

The Euler-Lagrange equation corresponding to equation (5) has the usual first integral

$$\frac{1}{2} \theta'^2 = -\frac{1}{2} p \theta^2 + \frac{1}{4} q \theta^4 + \frac{1}{2} p \theta_m^2 - \frac{1}{4} q \theta_m^4$$

(A.1)

with $\pm \theta_m$ the turning points for motion in the anharmonic potential $U(\theta)$ of the equivalent dynamical problem, that is points where $\theta' = 0$, and where in dynamics $\theta' = \partial \theta / \partial t$. 

---

Fig. 4. — The free energy $F_{\text{tot}}(\eta)$ versus the order parameter $\eta$ for strains $p/p_c = 3$ (curve a), 3.5 (curve b), 4.10 (the transition point, curve c) and 5 (curve d).
If the amplitude \( \theta_m \) of "oscillations" of the particle is exactly from one maximum \( \theta_0 = \sqrt{p/q} \) of \( U(\theta) \) to the other. \(-\theta_0\), then the period of the motion is infinite. For smaller amplitudes \( \theta_m < \theta_0 \) the period \( d \) remains finite. Factorizing the first integral above yields \( \theta'^2 = \frac{1}{2} q(\theta^2_m - \theta^2)/(2\theta^2_0 - \theta^2 - \theta^2) \) which can be integrated to:

\[
\int_0^T du = \int_{\theta_m}^{\theta_0} \sqrt{\frac{2}{q} \frac{\theta^2_m - \theta^2}{\sqrt{2\theta^2_0 - \theta^2 - \theta^2}}} \frac{d\theta}{\sqrt{\theta^2_m - \theta^2}}.
\]

where \( u = x/\xi \) and \( T \) is the reduced period \( d/\xi \). To make the elliptic integral obvious, we change variables \( \theta = \theta_m t \), extract constants \( 2\theta^2_0 - \theta^2_0 \) and \( \theta^2_0 \) from the two roots in the denominator, denote \( \theta_m/\theta_0 = \eta \) (the amplitude reduced by its value at the infinite-period hyperbolic-tangent limit), and let \( k^2 = \eta^2/(2 - \eta^2) \). Then

\[
T = \frac{4}{\sqrt{q\theta_0}} \sqrt{\frac{2}{2 - \eta^2}} \int_0^1 \frac{dt}{\sqrt{1 - t^2}} = \frac{4}{\sqrt{p(2 - \eta^2)}} K(k^2),
\]

where \( K(k^2) \) is a complete elliptic integral of the first kind. For an arbitrary position on the oscillation cycle \( u \), not the full period, we have for the reduced angle \( t \): \( u = (x/\xi)\sqrt{p(2 - \eta^2)}/2 \), and \( k^2 \) is the standard modulus of elliptic functions.

The total free energy, \( F_{\text{tot}} \), given by the bulk equation (5) and the end-energy, requires the substitution of elliptic functions for \( \theta(v) \) and yields:

\[
F_{\text{tot}} = \frac{A\gamma p^{3/2}}{2\sqrt{2} q}(2 - \eta^2)^{1/2}\eta^2
\]

\[
\times \int_0^2 \sqrt{p(2 - \eta^2)/2} \left[ \frac{\eta^2}{2 - \eta^2} \left( 1 - \left( \frac{\eta}{p} \right)^{3/2} \frac{K}{\sqrt{2 - \eta^2}} \right) \right] sn^2 v + \frac{\eta^2}{2 - \eta^2} sn^4 v, \tag{A.2}
\]
where \( p \), effectively the strain relative to \( \lambda_1 \), has been reduced by a characteristic strain
\[
p_c = \left( 4 \frac{\xi}{\nu} \left( \frac{\nu}{\nu-1} \right)^2 \right)^{2/3}
\]
These integrals can be evaluated analytically. To do this we first reduce the \( \text{sn}^2 \) and \( \text{sn}^4 \) terms to \( \text{sn}^2 \) by using the identities
\[
\text{sn}'(z) = \text{cn} \text{dn},
\]
\[
\text{dn} = k \text{sn}.
\]
It is sufficient to integrate over half a period, between \( \varphi = 0 \) and \( 2K \), and to multiply the result by the number of half periods in \( L_\varphi \). The integrals in question are then
\[
\int_0^{2K} d\varphi k^2 \text{sn}^4 \varphi = \frac{1}{3} \left( 2(1 + k^2) \int_0^{2K} d\varphi \text{sn}^2 \varphi - 2K \right)
\]
and
\[
\int_0^{2K} d\varphi \text{sn}^2 \varphi = \frac{2}{\sqrt{k}}(K - E),
\]
where \( E(k^2) \) is a complete elliptic integral of the second kind. Assembling these integrals, and the prefactors from equation (A.2) and the number of half-periods (using \( \pi / (\xi \equiv \mu) \)), one obtains
\[
F_{\text{tot}} = \frac{V \mu p^2}{2} \frac{1}{q (1 + k^2)^2} \left( \frac{2}{3} [k^2 K - 2(1 + k^2)(K - E)] + \left( \frac{p_c}{p} \right)^{3/2} 2(1 + k^2)^{3/2} K(K - E) \right).
\]
This total free energy is plotted in Figure 4 as a function of the order parameter \( \eta = \left( \frac{2k^2}{1 + k^2} \right)^{1/2} \), for several characteristic values of the reduced parameter \( (p/p_c) \). It is particularly important to verify that the transition in \( \eta(p) \) is always of the first order. To check this one may expand the full free energy \( F_{\text{tot}} \) in power series around \( \eta = 0 \) (such a Landau expansion is not suitable to describe the actual transition with a jump to \( \eta \sim 0.9 \), but serves to illustrate the presence of an energy barrier):
\[
F_{\text{tot}} \approx \frac{V \mu p^2}{2} q \left[ \frac{\pi}{4} \left( \frac{p_c}{p} \right)^{3/2} \eta^2 - \frac{7\pi}{64} \left( \frac{12}{7\pi} - \left( \frac{p_c}{p} \right)^{3/2} \right) \eta^4 + .. \right]
\]
At sufficiently large \( p \) the quartic-order coefficient is negative, but the square-order term is always of positive sign.

Although the nature, and the position of the transition are evident in Figure 4, one can obtain an explicit analytical dependence of the order parameter, \( \eta(p) \). Using the differential properties of complete elliptic integrals, it is straightforward to minimize \( dF_{\text{tot}}/dk^2 = 0 \) and
to obtain the converse relation:

$$\left( \frac{p}{p_c} \right)^{3/2} = \frac{3 k^2 (1 + k^2)^{3/2} K^2 (2 E - K + k^2 K)}{2 (E + k^2 E - K + k^2 K)^2}$$

From this closed expression we plot the variation of the order parameter $\eta$ and the modulus $k^2$, which controls the degree of coarsening of the domain-wall solution $\theta(x)$. The point of the transition is obtained explicitly, from substituting the relation $p(k^2)$ back into the free energy and finding for the point where this optimized $F_{\text{tot}}^*(k^2) = 0$ (the curve c in Fig. 4). This condition reduces to an equation

$$-2E^3(1 + k^2)^2 + 2E^2K(3 + 4k^2 + k^4) - 2EK^2(3 + k^2 - k^6) + K^3(2 - 2k^2 + k^4 - k^6) = 0,$$

with the solution for the transition point $k^2 \approx 0.692$. giving $(p/p_c) \approx 4.108$ and $\eta \approx 0.904$.

References