Orientational order in systems with competing interactions

Daniel A Stariolo[1] and Daniel G Barci[2]

[1] Departamento de Física, Universidade Federal do Rio Grande do Sul and
National Institute of Science and Technology for Complex Systems
CP 15051, 91501-970 Porto Alegre, RS, Brazil
[2] Universidade do Estado do Rio de Janeiro, Rua São Francisco Xavier 524, 20550-013, Rio de Janeiro, RJ, Brazil

E-mail: `daniel.stariolo@ufrgs.br`

Abstract. Quasi two dimensional systems with competing interactions usually display complex patterns in the relevant order parameter. In many cases these patterns are analog to liquid-crystal phases, showing smectic, nematic or hexatic order. We show that order parameters suitable for the characterization of these phases in systems with nearly isotropic competing interactions emerge naturally from an analysis of a Landau model. We describe with some detail the nematic case, which characterizes orientational order of striped domain walls. The Landau model presents an isotropic-nematic transition of the Kosterlitz-Thouless type. Although for the perfectly isotropic model long range nematic order is absent in infinite systems, we show that in real systems of finite size nematic order of domain walls can be observed.

1. Introduction

In many natural systems complex patterns originate due to the presence of competing interactions at different scales. Examples range from classical systems like magnetic ultrathin films [1], diblock copolymers [2] and colloidal suspensions [3], to quantum systems like quantum Hall samples [4] and high T_c superconductors [5]. These pattern forming systems may present positional as well as orientational order, the origin of which depends on microscopic interactions. In the case of magnetic ultrathin films, of a few atomic monolayers thick, strong anisotropy perpendicular to the film plane forces the magnetization to be out of plane. In this case short range ferromagnetic interaction competes with antiferromagnetic dipolar interaction. As a consequence, the system shows ordered striped phases, of alternating magnetization along one direction, as is seen in Figure 1.

In Figure 2 similar patterns can be observed in a completely different system, a block copolymer. In this case, elongated polymer chains with different types of building "blocks" compete between them and produce phase segregation, giving rise to complex patterns in two and three dimensions.

Figure 3 shows a schematic representation of microemulsion phases. Microemulsions are mixtures of anfiphilic molecules which have an hydrophilic head and an hydrophobic tail. When in contact with water and oil, as depicted in the figure, they tend to phase separate giving rise to different kinds of ordered patterns with an order similar to liquid crystals [7, 8].
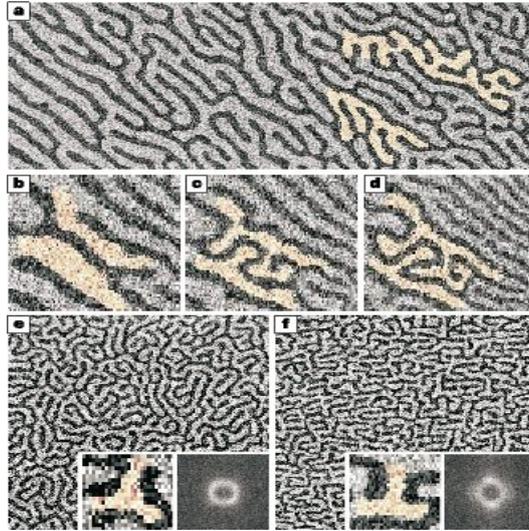
Figure 1. Fe/Cu(001) ultrathin films. The images, taken with scanning electron microscopy with polarization analysis (SEMPA), show a sequence of characteristic patterns and topological defects. From [1].
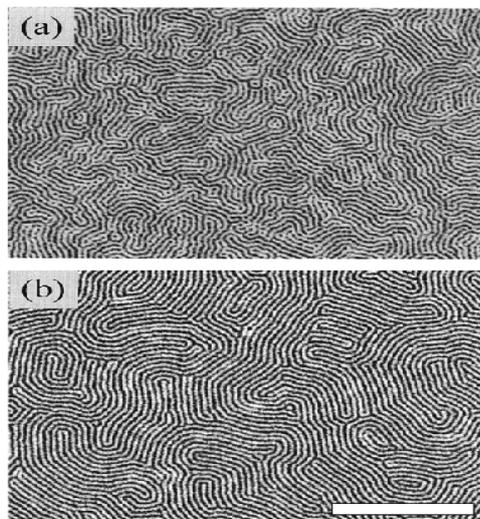
Figure 2. SBS block copolymers annealed on a bare silicon wafer and a PS brush-coated wafer respectively. From [6].

The equilibrium pattern in these systems depends in general in details of the interactions, like anisotropies, anchoring with a substrate, whether interactions are short or long range. Usually the kinematics shows several well defined time scales, and the ultimate equilibrium pattern is difficult to attain due to very long relaxation times. Despite these important characteristics, even the ideal equilibrium phases in simple situations are poorly understood. In general, there is a characteristic temperature T_C where the system begins to phase separate and a characteristic length scale sets in, usually called the modulation length, l_m. Below this characteristic temperature the equilibrium pattern adopts a labyrinth-like structure, like in
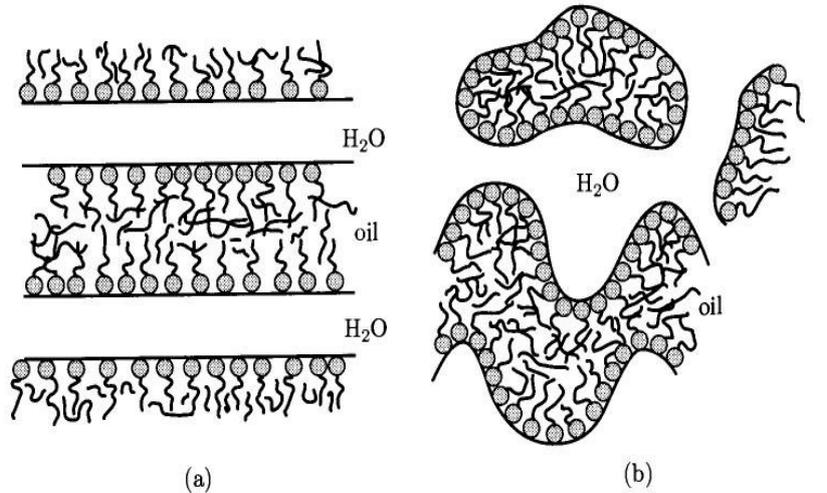
Figure 3. (a) A lamellar microemulsion phase with water, oil and surfactant layers. (b) Schematic representation of a random bicontinuous phase in which there is a random surfactant surface separating oil and water regions. From [9].

Figure 2. These patterns show neither positional nor orientational order, but a well defined stripe-like structure with a characteristic modulation length is easily recognized. Upon further lowering temperature or changing concentration of one species orientational order of the stripes begins to be observed at a temperature T_N. Domains of elongated stripes form and a new characteristic length appears in the system, l_s. Locally positional order develops together with orientational order of stripe domains walls. This regime may show long range orientational order but only short range positional order. In the presence of anisotropies or anchoring a further transition to a state with full positional order can happen at a temperature T_S.

Although this phenomenology is well known, the theoretical description of this sequence of phase transitions and the changing orders associated with them is usually done in terms of analysis of elasticity of domain walls [10, 11] instead of, e.g. microscopic approaches. A long time ago Brazovskii [12] proposed a Landau-type model for systems with nearly isotropic competing interactions. He obtained the important result that, although the Landau expansion in the model had only square and quartic powers of the order parameter, a first order phase transition induced by fluctuations was observed, contrary to what could be expected a priory. The essential feature behind this behavior is that the dominant low energy mode is not the usual $k = 0$ one, but a mode with $k \neq 0$, which in fact defines the modulation length of the order parameter. Brazovskii's analysis had a strong influence on subsequent work on these kind of systems, for example in explaining the low temperature behaviour of diblock copolymers [13] and the also well known Swift-Hohenberg model for the onset of instability in Raleigh-Bénard convection [14, 15]. Nevertheless, analysis of the Brazovskii's model were limited to the isotropic-stripe transition, which was the last one described above in the possible sequence of phase changes. The low temperature stripes or modulated phase is strongly unstable in two dimensions, as recognized long time ago by Swift and Hohenberg [14]. Nevertheless, stripes with long range orientational order are seen in experiments in many different systems belonging to the Brazovskii class. Clearly, a more comprehensive theoretical description of orientational phases in systems with isotropic or nearly isotropic competing interactions is needed.

An extension of the Brazovskii model, capable of describing phases with orientational but

not necessarily positional order, has recently been discussed by us [16, 17]. We have identified a suitable order parameter of domain wall orientation, similar to the director of nematic liquid crystals. Interestingly, this order parameter emerges naturally from a proper analysis of the Landau expansion for the kind of systems of the Brazovskii class. The resulting Landau free energy describes the two relevant transitions from isotropic to nematic and from nematic to stripes, in agreement with experimental observations.

Here we first describe a nematic-like order parameter suitable for quantifying orientational order of domain walls in two dimensional stripe-forming systems. Then we outline the derivation of a Landau free energy where this order parameter emerges naturally from symmetry considerations. We present and discuss the results of a mean field calculation of this free energy and show that the model has a nematic-isotropic second order phase transition [16]. The consequences of fluctuations around the mean field solution are also discussed [17]. We show that, although in two dimensional systems with isotropic competing interactions there is no true long range nematic order, in typical experimental scales nematic long range order can be observed.

2. The nematic order parameter
The kind of order we want to describe is exemplified in Figure 4.
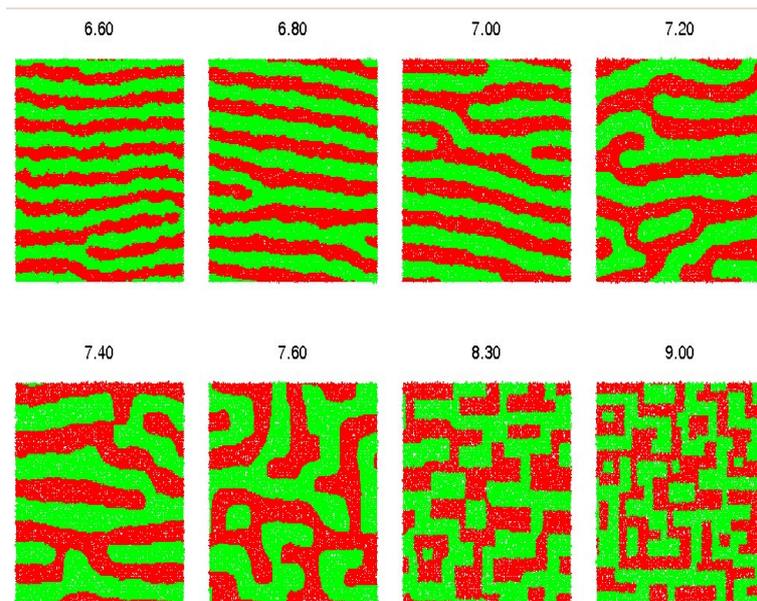
Figure 4. Computer simulation of the temperature evolution of patterns in a two dimensional Heisenberg ferromagnet with perpendicular anisotropy and competing dipolar interactions [18].

Competition between short range attraction and long range repulsion, or short range ferromagnetic and long range antiferromagnetic interactions usually gives rise to stripe-like patterns of the order parameter, which is generically represented by a density or magnetization $\phi(\vec{x})$.

Domain walls are observed at the transitions between positive and negative values of the order parameter. In order to quantify the degree of orientation of domain walls one can define the *director field*, defined as the gradient of the order parameter:

$$\mathbf{N}(\vec{x}) \equiv \nabla\phi(\vec{x}) = (\partial_x\phi, \partial_y\phi) \tag{1}$$
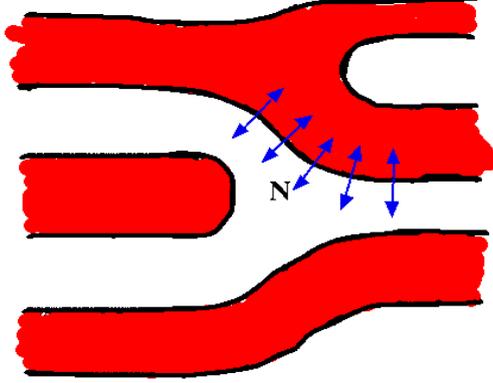
Figure 5. Schematic representation of a stripe phase with a dislocation. The arrows represent the director field, which is a local measure of orientation of domain walls.

Defined in this way the director is a vector which defines a vector field over the area of the two dimensional system. But this is not exactly the kind of order parameter we are seeking for. It is clear from Figure 5 that orientational order does not depend on up-down or left-right vector directions, both orientations along the perpendicular to the domain walls are equivalent. One way to incorporate this symmetry is to define a *tensor* order parameter, similar to the tensor order parameter of nematic liquid-crystals. In terms of the gradient of the density ϕ, the local tensor order parameter is defined as:

$$Q_{ij}(\vec{x}) \equiv \phi(\vec{x}) \left(\partial_i \partial_j - \frac{1}{2} \partial^2 \delta_{ij} \right) \phi(\vec{x}), \tag{2}$$

where $i, j = \{x, y\}$. This tensor is symmetric and traceless, and in two dimensions it has only two independent elements, which essentially represent the mean orientation of domain walls and the strength of the orientational order.

In order to get some feeling of the physical content of this order parameter it is useful to write it in reciprocal space. Introducing the Fourier transforms:

$$\tilde{Q}_{ij}(\vec{k}) = \int d^2x \, Q_{ij}(\vec{x}) \, e^{-i\vec{k}\cdot\vec{x}} \qquad\qquad Q_{ij}(\vec{x}) = \int \frac{d^2k}{(2\pi)^2} \, \tilde{Q}_{ij}(\vec{k}) \, e^{i\vec{k}\cdot\vec{x}}, \tag{3}$$

we get

$$\tilde{Q}_{ij}(\vec{k}') = \int d^2k \left(k_i k_j - \frac{1}{2} k^2 \delta_{ij} \right) \tilde{\phi}(\vec{k}) \tilde{\phi}(\vec{k}' - \vec{k}) \tag{4}$$

The mean global order parameter is given by:

$$
\begin{aligned}
\langle Q_{ij} \rangle &= \int d^2x \, Q_{ij}(\vec{x}) = \langle \tilde{Q}_{ij}(\vec{k}' = 0) \rangle \\
&= \int d^2k \left(k_i k_j - \frac{1}{2} k^2 \delta_{ij} \right) \langle \tilde{\phi}(\vec{k}) \tilde{\phi}(-\vec{k}) \rangle
\end{aligned}
\tag{5}
$$

Choosing the x-axis as the principal axis, the only relevant element of the tensor is:

$$\langle Q_{xx} \rangle = \int d^2k \, k^2 \, \cos(2\theta) \, C(\vec{k}) \tag{6}$$

where $k_x = k\cos\theta$ and $k_y = k\sin\theta$ and $C(\vec{k})$ is the structure factor of the system. Written in this way the orientational order parameter quantifies the degree of anisotropy of the domain pattern. In a completely isotropic phase, for example a liquid phase or a mosaic of domains with no preferential direction, the corresponding isotropy in the structure factor will be reflected in a zero value of the orientational order parameter. This is illustrated in Figure 6.
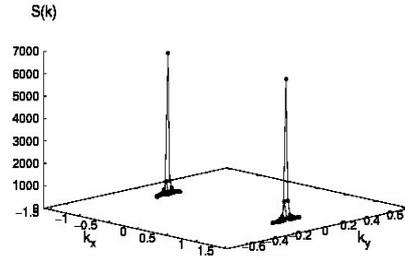
$$\langle Q \rangle \sim 1$$
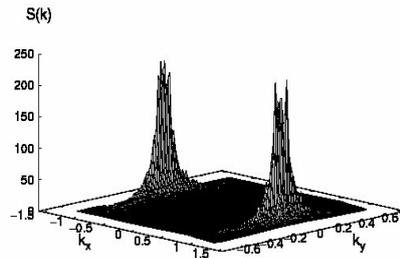
$$\langle Q \rangle \sim 0.8$$
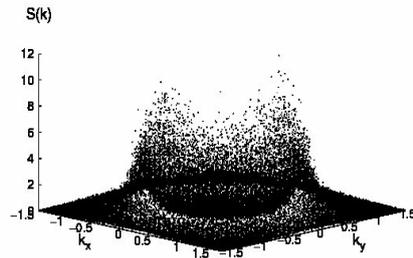
$$\langle Q \rangle \sim 0.1$$

Figure 6. Structure factor of a model with competing exchange and dipolar interactions in $d = 2$ for three different temperatures. The pictures from top to bottom are characteristic of the stripes, nematic and isotropic phases respectively. Taken from [19].

The three figures represent the structure factor of a model for ultrathin magnetic films with strong perpendicular anisotropy, which has short range ferromagnetic interactions competing with long range dipolar interactions [19]. The top figure shows $C(\vec{k})$ for a very low temperature, where the equilibrium state of the system presents almost perfectly straight stripes of up and down magnetization. $C(\vec{k})$ presents two very narrow peaks at a wave vector corresponding to the modulation length of the stripes. The system has both orientational and positional order. The second figure corresponds to a higher temperature. The two peaks are considerably broaden and positional order has been lost. Nevertheless orientational order is still present, as confirmed by the high value of the tensor order parameter $\langle Q \rangle \approx 0.8$. This corresponds to a nematic-like phase. The third figure shows an almost rotationally invariant structure factor. This isotropy reflects an absence of orientational order and corresponds to a disordered high temperature phase.

3. The extended Brazovskii model

The dominance of a mode with a non-zero wave vector at low energies can be studied through a phenomenological model of the Landau-Ginzburg type, first analyzed by Brazovskii [12]:

$$\mathcal{H} = \int \frac{d^2k}{(2\pi)^2} \, \phi(\vec{k}) \left(r_0 + \frac{1}{m} \, (k - k_0)^2 + \dots \right) \phi(-\vec{k}) +$$

$$+ \, u_0 \int \frac{d^2k_1}{(2\pi)^2} \frac{d^2k_2}{(2\pi)^2} \frac{d^2k_3}{(2\pi)^2} \frac{d^2k_4}{(2\pi)^2} \, \phi(\vec{k}_1)\phi(\vec{k}_2)\phi(\vec{k}_3)\phi(\vec{k}_4) \, \delta(\vec{k}_1 + \vec{k}_2 + \vec{k}_3 + \vec{k}_4) \qquad (7)$$

This model, when considered at mean field level, gives rise to a isotropic-stripes transition which is second order. Below T_c the order parameter varies in a sinusoidal way:

$$\phi(\vec{x}) = A \, \cos{(\vec{k}_0 \cdot \vec{x})}. \qquad (8)$$

Brazovskii showed that including fluctuations in a self-consistent way, the model leads to a first order phase transition induced by fluctuations. The low temperature striped phase, dominated by a mode with k_0 wave vector, has positional long range order in the form of two symmetric delta function peaks in the structure factor, at least near the transition. At lower temperatures other modes come into play and the profile of the order parameter changes developing sharp domain walls as $T \to 0$. Although applied to some two dimensional systems, it is known that the low temperature stripe phase is strongly unstable in this case. Angular fluctuations of the dominant wave vector of modulus k_0 does not cost energy, as shown in Figure 7. Some kind of anisotropy in the interactions or pinning to a substrate are necessary in order to stabilize the phase.

Nevertheless, it was recently shown that orientational order of domain walls can persist even in the case of ideal isotropic interactions [16, 17]. Let's analyze the implications of isotropy for the interaction term, which in general will be a function $u(\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4)$, with wave vectors k_1, k_2, k_3 and k_4 as shown in Figure 7:

- Isotropy forces the wave vectors to lay on a circle of radius k_0 and hence $u(\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4) = u(\theta_1, \theta_2, \theta_3, \theta_4)$.
- Conservation of total momentum allows to eliminate one of the four $k's$.
- Fixing two of them, the other two are automatically fixed by the requirement that the four vectors lay on the circle.
- Because of rotational invariance, the interaction can only depend on the difference between the two independent angles:

$$u(\theta_1, \theta_2, \theta_1 + \pi, \theta_2 + \pi) = u(\theta_1 - \theta_2) = u(\theta)$$
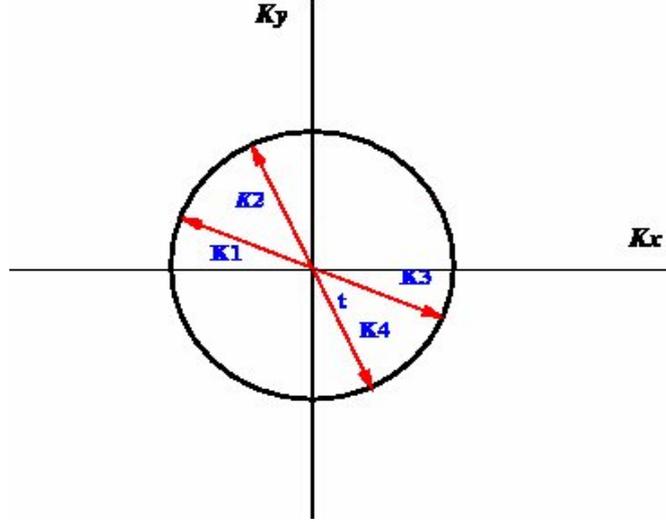
Figure 7. The wave vectors present in the quartic interaction term must lie on a circle of radius k_0 for perfectly isotropic interactions. This fact alone determine the form of the quartic term of the Landau expansion, as explained in the text.

- Finally, index permutation invariance in $u(\vec{k}_1, \vec{k}_2, \vec{k}_3, \vec{k}_4)$ implies $u(\theta) = u(\theta + \pi)$, then u can be expanded in Fourier series:

$$u(\theta) = u_0 + u_2 \cos(2\theta) + u_4 \cos(4\theta) + \ldots \tag{9}$$

In the previous expression for the interaction we recognize the first, constant term, as that present in the original Brazovskii's model, eq. (7). But symmetry considerations led us to conclude that an infinite number of additional terms must be considered in the expansion, and it turns that all of them are relevant in a Renormalization Group sense [16]. From the form of eq. (9) one sees that all the cosine terms share a nematic symmetry, i.e. they are invariant with respect to rotations $\theta \to \theta + \pi$. Keeping the first two terms, we can rewrite the Brazovskii energy in the form:

$$\mathcal{H} = \mathcal{H}_{Br} + u_2 \int \frac{d^2k}{(2\pi)^2} Tr \, \tilde{Q}^2, \tag{10}$$

where $\mathcal{H}_{Br}$ is given by (7), $Tr\, \tilde{Q}^2$ is the trace of the nematic tensor squared, and $\tilde{Q}_{ij}(\vec{k})$ is given by eq. (4).

An analysis of this Hamiltonian in the self-consistent or Hartree approximation gives the following results [16, 17]:

- If $u_2 = 0$ we recover the Brazovskii's Hamiltonian, which has a low temperature smectic phase with a stripe-isotropic first order transition induced by fluctuations. In two dimensions this solution is unstable, and then $T_{Br} \to 0$.

- If $u_2 > 0$ the nematic term has a repulsive character, and the only possible solution for the nematic order parameter is $\langle Q(T) \rangle = 0$.

- When $u_2 < 0$ the nematic energy is attractive and the model shows a *nematic-isotropic* phase transition. The transition is second order in the mean field approximation, with $\langle Q(T) \rangle \propto (T_c - T)^{1/2}$ and the critical temperature is given by $T_c = 2/(mk_0^2) \sqrt{u_0/|u_2|}$.

A representation of the mean field phase diagram for the extended model can be seen in Figure 8. We see that the stripe phase is depressed to zero temperature. This is because

of strong fluctuations in the orientation of the dominant wave vector k_0 in two dimensions. In reference [20] a criticism to the results in [16] was raised, based on the fact that the stripe solution is strongly unstable for isotropic interactions in two dimensions. In the reply to that comment [21] we clarified the controversy, which was probably funded in a misinterpretation of our main conclusion, i.e. the existence of a *nematic* phase with a finite critical temperature, in addition to the stripe (smectic-like) phase which is depressed to zero temperature as a consequence of fluctuations. As we said before, this fluctuations can be made weaker by means of anisotropies originated e.g. by an underlying lattice which breaks rotational symmetry. In this case it is expected that T_{Br} will have a finite value.
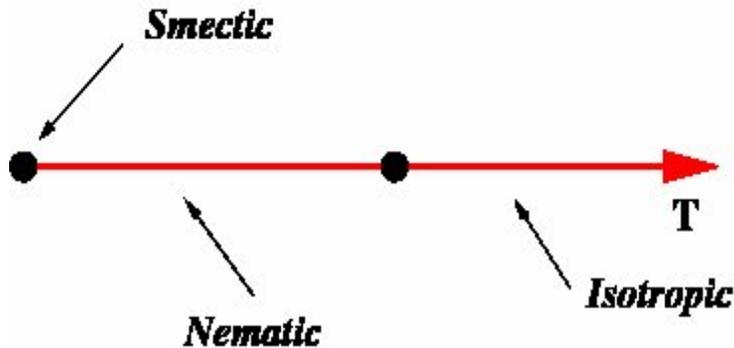
Figure 8. Mean field phase diagram of model (10).

We must also consider the effect of fluctuations on the mean field nematic solution. Considering Gaussian fluctuations around the saddle point solution we arrive to a correction term contributing to the free energy of the form [17]:

$$\delta F = \rho_s(T) \int d^2x \, |\vec{\nabla}\varphi(\vec{x})|^2, \tag{11}$$

where $\varphi(\vec{x})$ represents angular fluctuations of the director and $\rho_s(T)$ is the temperature dependent stiffness. This free energy term has the form of the two dimensional XY model, and then shares all of its physical properties. In particular it implies that the phase transition is of the Kosterlitz-Thouless type [22]. The low temperature nematic phase has not true long range order, because correlations decay algebraically. Instead, it presents *quasi-long-range order*. In particular, the nematic order parameter is depressed below its mean field value in a way given by:

$$\langle Q \rangle = \langle Q \rangle_{MF} \, \exp(-W) \tag{12}$$

with

$$W = \frac{T}{4\pi\rho_s} \ln\left(\frac{L}{a}\right), \tag{13}$$

where L is the linear dimension of the system and a a microscopic interparticle distance. It is then clear that in the thermodynamic limit $L/a \to \infty$ we have $\langle Q(T) \rangle \to 0$ logarithmically, and the there is no long range order at any finite temperature. Nevertheless, in some real systems, the actual situation if far from the ideal thermodynamic limit. For example, in ultrathin films of *Fe/Cu(001)* studied in [1] typical scales are $L \approx 10^{-3}m$ and $a \approx 10^{-10}m$. At room temperature, where most of the experiments are done, $W \approx 7/32$ and then $\langle Q \rangle \approx 0.8 \langle Q \rangle_{MF}$. Our conclusion is that, even in cases with perfectly isotropic interactions it is possible to observe a low temperature nematic phase, with long range order up to the scales characteristic of many experimental samples. The experimental characterization of these orientational phases in diverse systems as magnetic ultrathin films, block copolymers and microemulsions is an important challenge.

4. Perspectives

We showed that the emergence and evolution with temperature of systems forming striped-like patterns can be conveniently described by an effective free energy which incorporates a nematic-like order parameter in a Landau expansion. This leads to a new perspective on the low temperature phases of two dimensional systems with competing isotropic interactions.

Many points remain to be clarified, we conclude by enumerating some of them:

- Is it possible to identify a *microscopic* origin for the phenomenological nematic term ? or in other words, what kind of microscopic Hamiltonians can give rise to the phenomenology described by the present Landau model ?

- What is the real importance of the other (infinite) terms in the expansion of quartic coupling function ? Can this question be answered by a RG analysis ?

- What are the effects of adding anisotropies on the low temperature phase of the systems ? What are the effects of confining or limiting lateral dimensions ?

- Are these equilibrium properties important from a dynamical perspective ? What is the nature of the relaxation dynamics of these pattern forming systems ?

We think that all these important questions are still to a great extent unresolved.

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