SPECIAL TOPICS

Physics of Soft Condensed Matter

JPSJ PROOF

Defect Dynamics in Mesophases

Jorge VIÑALS

Department of Physics, McGill University, Montreal, QC H3A 2T8, Canada

Block copolymer phases are a fertile ground in which to investigate both equilibrium and nonequilibrium properties of mesophases (phases that exhibit partial broken symmetries, intermediate between a completely disordered fluid and a perfectly order crystal). We focus here on two particular phases: a lamellar phase (of smectic symmetry, solid like in one direction and fluid in the two other directions), and a columnar phase (a hexagonal solid in two dimensions, and fluid in the third dimension). Starting from a mesoscopic model of the copolymer, we present the amplitude equations of motion for tilt and twist grain boundaries, and the resulting equations of motion for slightly distorted boundaries. We also examine the assumptions underlying the separation of scales in the derivation of the amplitude equations, and analyze corrections to the equations due to the coupling to the $\mathcal{O}(1)$ variation of the order parameter in the vicinity of the boundaries. These corrections can lead to defect pinning. The effect of pinning on defect motion depends on whether the bifurcation originating the mesophase is super or sub critical.

1. Introduction

Macromolecular self assembly of block copolymer mesophases is being actively investigated for the development of a wide variety of nanostructured materials, or as templates, also at the nanoscale.[1] Spontaneous self assembly, for example, provides an alternative route to conventional lithography, potentially allowing features in the sub-15 nm range, while retaining the reliability and mass production ease that are required in the semiconductor industry.[2–4] High density storage devices that are built on block-copolymer templates are also being investigated[5] by creating small magnetic wires held by a block copolymer matrix. The density of wires is high enough that if each post could be addressed individually, a maximum storage density of 1 Tb/cm^2 of material could be achieved.[6] A third different realm of applications is based on the periodic variation of the index of refraction in a macroscopically order copolymer, leading to the production of photonic band gap materials by using polymer chains of fairly standard length.[7,8]

While copolymer self assembly is quite efficient at creating locally ordered configurations at the nanometer scale, achieving long range order over macroscopic distances is very difficult. Macroscopically, samples are generically disordered because they contain a large number of defects. Such disordered samples are not suitable for the applications outlined above. Controlling the long range microstructure of bulk block copolymer samples or thin films is therefore the central challenge that needs to be overcome before widespread use of this material can be contemplated.[9–13]

A number of strategies have been put forward to accelerate annealing of defects, or to post process polycrystalline samples in order to increase the characteristic size of ordered domains. Steady and oscillatory shear flows have been applied with some success,[14–18] although the mechanisms leading to the selection of a particular orientation of the copolymer relative to the imposed shear are not yet well understood.[19] Graphoepitaxy is another of the strategies being used to control long range order of block copolymer microphases.[20,21] Topographic relief on a substrate orients the subsequent epitaxial growth of a deposited copolymer film. Very long surface areas (on the mm scale) have been successfully patterned by this technique. Electric fields (dc) have also been proven successful in orienting multi domain or polycrystalline samples in both lamellar and cylindrical phases.[22] Through coupling with the dielectric constant contrast of the monomers in each microphase domain, both grain boundary migration (close to the order disorder temperature) and grain rotation (away from it) are the mechanisms observed that mediate the establishment of long range order. Solvent annealing is another promising avenue to produce long range order in films.[23] By externally controlling the rate of solvent evaporation, a particular orientation of the growing microdomains can be favored, and one can even rearrange already formed grains. Large enough ordered samples can be produced to study structural transitions in two dimensional films. A similar strategy involves the controlled use of zone annealing by inducing localized melting and reordering (along the lines of zone refinement techniques for crystal growth). The sample is placed under a uniform temperature gradient, and the development of microphase separated domains occurs at a moving front separating cold and hot regions. This controlled ordering process appears to limit the number of defects that are incorporated into the microphase separated phase.[24] Effort is also being devoted to controlling long range order through chemically patterning the substrate on which the block copolymer film will be deposited.[25] Patterns of greatly improved uniformity (lack of defects) as well as extent have been produced. We finally mention efforts to address the formation or ordered structures in mixtures of block copolymers and nanoparticles.[26,27] The propensity of both to form ordered structures, and their

coupling, has been argued to favor the emergence of hierarchically ordered structures. Nanoparticles segregate to the boundaries of ordered grains, and through modification of the interfacial energetics, favors the reorientation of copolymer molecules adjacent to the boundary. The potential advantage of this method is that it does not require the use of any external fields.

In parallel to this extensive experimental research program into microstructure formation and evolution in block copolymers, significant progress has been achieved in our theoretical understanding of defect motion and microstructure coarsening, both by analytic and numerical means. We will focus below on a mesoscopic description of the block copolymer following the pioneering work of Leibler[28] and Ohta and Kawasaki.[29] At frequencies low compared with the inverse relaxation time of the polymer, chain conformation effects can be adiabatically eliminated, and a mesoscopic theory in terms of the monomer composition alone can be developed. Significant effort has been devoted recently into incorporating more detail into this mesoscopic theory arising from the architecture of the polymers. This has led to complex self consistent field theory formulations in equilibrium,[30,31] and to extensions to time dependent dynamics at the mean field level (dynamic density functional theory).[32]

Early theoretical studies of defect motion from a mesoscale model include a calculation of dislocation climb velocities by Siggia and Zippelius,[33] and the motion of grain boundaries in lamellar (or stripe) phases by Tesauro and Cross.[34] A central assumption in these treatments is that close to onset (the order disorder transition temperature in the case of a block copolymer), the order parameter field admits a multiple scale expansion so that the defect can be treated as a point or line of singularity. If ϵ is the dimensionless distance away from threshold, the extent of the defect scales as an inverse power of ϵ in the limit $\epsilon \to 0$. The underlying assumption is that details of the physical processes near defect cores (not explicitly included in the mesoscopic description) are unimportant for defect motion, the latter being controlled by the far field envelope of the order parameter. These observations form the basis of the analysis of defect motion presented below. We will also critically examine the asymptotic methods uses to decouple short scale phenomena in the defect region from the long scale motion of the order parameter envelope, and its contributions to defect pinning and effective coarsening rates. We will, in particular, argue that non adiabatic effects (effects arising from the coupling between the two scales) are asymptotically small at a supercritical bifurcation, but remain finite in the subcritical case.

A recent comprehensive study of defect motion and microstructure coarsening has address the emergence of long range order in a thin film of polystyrene–polyisoprene (PS–PI) in the cylindrical phase.[35] Since the cylinders in this system lie parallel to the substrate, stripe patters are observed. A large number of defects are formed early on, which anneal away as the sample approaches equilibrium. Disclinations are the longest lived defects observed, and hence their motion and mutual annihilation controls the evolution of the system towards macroscopic equilibrium. The particular mechanism of defect annihilation involves

quadrupolar disclination arrangements so that dimensional arguments lead to a coarsening rate for the linear scale of the structure as $l(t) \sim t^{1/4}$. This behavior has been indeed observed in the experiments where $l(t)$ is proportional to the orientation correlation length of the cylinders. This study has been later extended to thin films of PS–PI in the spherical phase (the ordered structure in this case is of hexagonal symmetry).[36] Whereas growth in orientation correlations also appears to be a power law with exponent equal 1/4, other scales measuring defect separations obey slower growth rates. It is also observed in this case that defect velocities are strongly dependent on temperature, and related numerical analysis has revealed that defect motion stops at very low temperature.[37] Anomalous defect motion at low temperatures in hexagonal phases was already addressed by Sagui and Desai.[38]

Additional research has focused on the short scale structure and motion of defects. Combined experimental (scanning force microscopy) and numerical calculations (self consistent dynamical mean field theory) have revealed the strong correlation between defect structure and local chain mobility.[39] Chain correlations induced by monomer bonds affect the details of propagation of structural defects. Similar microscopic studies have been conducted on twist grain boundaries,[40] also by dynamical mean field theory. In this particular case, insight is gained into the short scale mechanics of chain motion that mediate defect motion to show that only diffusion parallel to the grain boundary is necessary for its motion. The thickness of the grain boundary observed is very small, of similar order to the lamellar spacing. A study that is intermediate between these later studies and the mesoscale approaches described above concerns the analysis of the isotropic-smectic A transition[41] in terms of the nematic tensor order parameter. Given that the symmetry of the high and low temperature phases is the same as in the case of microphase separation into a lamellar phase of a block copolymer, this study has also addressed some of the detailed aspects of defect structure and motion during coarsening. Generally the results are in agreement with those found in block copolymers in the lamellar phase:[35] Quadrupolar configurations of disclinations dominate in the coarsening regime. However, different measures of the linear scale of the structure $l(t)$ obey different growth laws, fact that calls into question the scaling (or dimensional) analyses used to derive these laws.

We focus below on a somewhat simpler problem, and derive the amplitude or envelope equations governing grain boundary motion from the Leibler free energy. We include both tilt and twist grain boundaries. We then reexamine the derivation of the amplitude equations, and discuss non adiabatic effects, pinning, and effective equations for defect motion.

2. Model Equations

For length scales much larger than the monomer persistence length, and time scales long enough compared with the longest polymer chain relaxation time, the evolution of a block copolymer melt can be described by an order parameter field $\psi(\boldsymbol{r}, t)$ which represents the local density difference of the constituent monomers, and a local velocity field $\boldsymbol{v}(\boldsymbol{r}, t)$. Given that relaxation of the concentration field

ψ is driven by local dissipation due to free energy minimization, one normally adopts the following time-dependent Ginzburg–Landau equation:[42]

$$\partial\psi/\partial t + \boldsymbol{v}\cdot\nabla\psi = -\Lambda\delta\mathcal{F}/\delta\psi, \tag{1}$$

where Λ is an Onsager kinetic operator (with $\Lambda = -M\nabla^2$ reflecting conserved dynamics for the order parameter. Given that in most cases short range diffusion of polymer chains is the only kinetic mechanism available in microphase separated samples, $\Lambda \simeq Mq_0^2$ and constant). In the cases discussed below, the advection term $(\boldsymbol{v}\cdot\nabla\psi)$ in eq. (1) will be neglected. The coarse-grained free energy functional $\mathcal{F}$ is given by the Ohta–Kawasaki energy.[29] In the weak segregation limit, however, (i.e., near the order–disorder transition point), a block copolymer melt can be described by a simpler coarse-grained free energy (the Brazovskii or Leibler energy)[28,42]

$$\mathcal{F}[\psi]$$
$$= \int \mathrm{d}\boldsymbol{r}\left\{-\frac{\tau}{2}\psi^2 - \frac{\tilde{g}}{3}\psi^3 + \frac{u}{4}\psi^4 + \frac{\zeta}{2}\left[(\nabla^2 + q_0^{*2})\psi\right]^2\right\}, \tag{2}$$

where the reduced temperature variable τ measures the distance from the order–disorder transition, with $\tau > 0$ for $T < T_{\mathrm{ODT}}$, and q_0^* is the wavenumber of the periodic structure. Note that here the order parameter has been replaced by $\psi \to \psi - \bar{\psi}$, the local deviation of the concentration field from its spatial average. Substituting eq. (2) into the Ginzburg–Landau equation (1), approximating Λ by Mq_0^{*2} which is valid near T_{ODT} with negligible long range diffusion, and rescaling all quantities to be dimensionless, we obtain the so-called Brazovskii or Swift–Hohenberg model equation

$$\partial\psi/\partial t = [\epsilon - (\nabla^2 + q_0^2)^2]\psi + g\psi^2 - \psi^3, \tag{3}$$

where $\epsilon = \tau/\zeta q_0^{*4}$ with $0 < \epsilon \ll 1$ corresponding to the weak segregation limit, $g = \tilde{g}/\sqrt{u\zeta q_0^{*4}}$, and $q_0 = 1$ after rescaling although we retain the symbol q_0 in what follows for clarity of presentation. For lamellar phases which correspond to symmetric block copolymers $(\bar{\psi} = 0)$ we have $g = 0$ in eq. (3).

Stationary solutions of eq. (3) are periodic, with wavenumber in the vicinity of q_0. Phases of different symmetries are possible; we focus here on lamellar phases (a single wave, $g = 0$), and hexagonal phases (three waves on a plane at $120°$, $g \neq 0$). Existence regions of the various phases, their stability against long wavelength perturbations, as well as their bulk relaxation modes have been studied extensively. We focus instead on the equations describing extended defects, such as grain boundaries, in order to understand the mechanisms involved in microstructure coarsening.

2.1 Tilt grain boundary

In the limit of weak segregation ($\epsilon \ll 1$), a multiple scale approach can be used to separate fast spatial and temporal scales [$\mathcal{O}(1)$] in ψ from slow modulations of its amplitude and phase.[34,43,44] For a three dimensional $90°$ grain boundary configuration comprising two lamellar domains of mutually perpendicular orientations (along $\hat{x}$ for domain A and $\hat{z}$ for domain B), the order parameter field can be written as the superposition of two base modes $\exp(iq_0 x)$ and $\exp(iq_0 z)$,

$$\psi = \frac{1}{\sqrt{3}}[A\exp(iq_0 x) + B\exp(iq_0 z) + \text{c.c.}], \tag{4}$$

with complex amplitudes A and B slowly varying in space and time:

$$A = A(X = \epsilon^{1/2}x, Y = \epsilon^{1/4}y, Z = \epsilon^{1/4}z, \epsilon t),$$
$$B = B(\bar{X} = \epsilon^{1/4}x, \bar{Y} = \epsilon^{1/4}y, \bar{Z} = \epsilon^{1/2}z, \epsilon t).$$

A standard multiple scale expansion leads to a coupled set of amplitude equations [at $\mathcal{O}(\epsilon^{3/2})$][44] that when rewritten in the original set of variables read,

$$\partial_t A = [\epsilon - (2iq_0\partial_x + \partial_y^2 + \partial_z^2)^2]A - |A|^2 A - 2|B|^2 A, \tag{5}$$

$$\partial_t B = [\epsilon - (\partial_x^2 + \partial_y^2 + 2iq_0\partial_z)^2]B - |B|^2 B - 2|A|^2 B. \tag{6}$$

For fixed ϵ, stationary bulk solutions in either domains A or B are periodic, with wavenumber near q_0. In a grain boundary configuration, on the other hand, the only stationary solution possible has wavenumber equal to q_0 (wavenumber selection). To this order in ϵ, the solutions for A and B do not depend on the fast scales (x, y, z). The stationary configuration is a planar boundary with both A and B changing quickly in the boundary region of extent $\xi \sim \epsilon^{-1/2}$.

A slightly distorted tilt grain boundary relaxes exponentially back to planarity with a rate $\sigma \propto q^4$ where q is the wavenumber of the distortion.[43] However, the average position of the boundary also advances with velocity,

$$v = \frac{\epsilon}{3q_0^2 D(\epsilon)}\kappa^2 \propto \frac{\kappa^2}{\epsilon}, \tag{7}$$

where $D(\epsilon)$ plays the role of a friction coefficient, and κ is the local mean curvature of the boundary. The motion is such that modulated stripes parallel to the boundary are always replaced by advancing perpendicular stripes. This asymmetry in the direction of motion of the boundary can be understood as due to the different elasticity of parallel and perpendicular stripes around the boundary, and the requirement that the global energy be minimized. As the boundary perturbation relaxes, so does the curvature (the driving force for motion) so that the boundary eventually stops. The total distance traveled is proportional to $\epsilon^{-1/2}$.

The implications of this result on domain coarsening have been addressed in.[45] If grain boundary motion is a relevant mechanism for coarsening of a lamellar phase, then eq. (7) implies a growth law $l(t) \sim t^{1/3}$. While this is observed in a direct numerical solution of the governing equation for sufficiently small ϵ,[45] it disagrees with the experiments of Harrison et al.[35]

2.2 Twist grain boundary

A twist grain boundary can be constructed by rotating two lamellar domains with respect to an axis perpendicular to the grain boundary plane, with lamellar normals of the two joint domains staying in a plane that is parallel to the boundary plane,

$$\psi = \frac{1}{\sqrt{3}}[A\exp(i\boldsymbol{q}_1\cdot\boldsymbol{r}) + B\exp(i\boldsymbol{q}_2\cdot\boldsymbol{r}) + \text{c.c.}], \tag{8}$$

where, for example, $\boldsymbol{q}_1 = q_0\hat{x}$ and $\boldsymbol{q}_2 = q_0(\cos\alpha\hat{x} + \sin\alpha\hat{y})$

(with α the twist angle) are the orientations of two domains adjacent the twist boundary. The evolution of the complex amplitudes A and B is governed by [to leading order in $\mathcal{O}(\epsilon^{3/2})$][46]

$$\partial_t A = [\epsilon - (\nabla^2_{\|_1} + 2iq_0\partial_{n_1})^2]A - |A|^2A - 2|B|^2A, \qquad (9)$$

$$\partial_t B = [\epsilon - (\nabla^2_{\|_2} + 2iq_0\partial_{n_2})^2]B - |B|^2B - 2|A|^2B, \qquad (10)$$

where n_1, n_2 are the normals to the lamellar planes in domains A and B respectively, $\nabla^2_{\|_1}$ is the the Laplacian operator on the lamellar plane of domain A, and $\nabla^2_{\|_2}$ represents the Laplacian operator on the lamellar plane of domain B. For instance, if $n_1 = \hat{x}$ (i.e., $q_1 = q_0\hat{x}$), $\nabla^2_{\|_1} = \partial^2_y + \partial^2_z$ and $\partial_{n_1} = \partial_x$. The difference between these amplitude equations and those for tilt grain boundaries given in eqs. (5) and (6) is due to the different relationship between domain orientations and the boundary plane in the two types of grain boundaries.

A simple dimensional analysis of eqs. (9) and (10) along the direction normal to the boundary yields $\xi \sim \epsilon^{-1/4}$ in contrast to the $\epsilon^{-1/2}$ result for a tilt grain boundary. Thus, in the limit of $\epsilon \to 0$, i.e., close to the order–disorder threshold, the width of a twist boundary region is much smaller than that of tilt boundary.

3. Scale Coupling and Non Adiabatic Corrections

The separation between scales of order one (x, y, z, t), and the slow scale of the modulation (X, Y, Z, T) is made explicit in developing the amplitude equations though assumptions such as $A = A(X = \epsilon^{1/2}x, Y = \epsilon^{1/4}y, Z = \epsilon^{1/4}z, \epsilon t)$. Of course, the expansion is checked for self-consistency order by order in ϵ. However, and following the original approach of Malomed *et al.*,[47] it is possible to estimate possible corrections to the amplitude equations if the amplitudes are assumed to retain a dependence in the fast variables (x, y, z). For the case of a tilt grain boundary separating two lamellar phases we find

$$\partial_t A = [\epsilon - (2iq_0\partial_x + \partial^2_y + \partial^2_z)^2]A - |A|^2A - 2|B|^2A$$
$$- \int_x^{x+\lambda_0} \frac{dx'}{\lambda_0} (A^3 e^{2iq_0x'} + A^{*3}e^{-4iq_0x'}), \qquad (11)$$

$$\partial_t B = [\epsilon - (\partial^2_x + \partial^2_y + 2iq_0\partial_z)^2]B - |B|^2B - 2|A|^2B$$
$$- \int_x^{x+\lambda_0} \frac{dx'}{\lambda_0} (A^2 B e^{2iq_0x'} + A^{*2}Be^{-2iq_0x'}), \qquad (12)$$

where $\lambda_0 = 2\pi/q_0$. Because the reference interface is planar and perpendicular to x, the undistorted envelopes A and B are only a function of x, and hence all terms in the solvability condition proportional to e^{iq_0y} integrate to zero. Note that the integrals in the right hand side would be zero if the amplitude is slow (constant) in the $\mathcal{O}(1)$ scale,[48] but it is possible to estimate their contribution otherwise. For example, the local normal velocity of a slightly perturbed grain boundary v is given by a double series expansion of the form,

$$D(\epsilon)v = T_1 + T_2 + \cdots + e^{-1/\sqrt{\epsilon}}\sin(2q_0x)(N_1 + N_2 + \cdots), \qquad (13)$$

where the terms T_i and N_i are proportional to powers of ϵ. Note that it is not possible in this case to obtain a solution in power series of ϵ alone, but rather there appear terms proportional to $e^{-1/\sqrt{\epsilon}}$. These terms vanish as $\epsilon \to 0$, but can

be quite large when ϵ is small but finite. In other words, if the amplitudes A and B are not exactly constant over the fast scale (say, over the thickness of the boundary), exponentially small terms appear in the amplitude equations. In essence, the equation for the slowly varying amplitudes cannot be decoupled from the phase of the defect. These new terms in the amplitude equation are called non adiabatic corrections as they originate in deviations from the adiabatic elimination of fast scales from the amplitude equation. Keeping only the lowest order terms (in ϵ) of both T_i and N_i, eq. (13) reads.

$$v = \frac{\epsilon}{3q_0^2 D(\epsilon)}\kappa^2 - \frac{p_L(\epsilon)}{D(\epsilon)}\cos(2q_0x_{gb} + \phi). \qquad (14)$$

where x_{gb} is the average location of the reference, unperturbed boundary, v its local normal velocity, and

$$p_L(\epsilon) \sim \epsilon^2 e^{-\alpha/\sqrt{\epsilon}}, \qquad (15)$$

with α a numerical constant. By comparing this equation to eq. (7) we notice that non adiabatic corrections add a new force to eq. (15) of amplitude p_L, and periodic as a function of the average location of the boundary x_{gb}. The pinning force depends on relative location of the phase of the defect and the $\mathcal{O}(1)$ variation of the order parameter.

Of course the dependence of p_L on ϵ follows immediately from the scaling of lengths with ϵ. A dependence that is proportional to $\epsilon^{-1/2}$ is generically expected near a supercritical bifurcation, as is the case considered involving a lamellar phase. It is possible to extend this calculation to the subcritical bifurcation that leads to a hexagonal phase[49] by considering $g \neq 0$ in eq. (3). If one considers a grain boundary separating two domains of hexagonal symmetry with relative misorientation θ, one can show that the non adiabatic contribution to the motion of the boundary is similar to the lamellar case, but with a different exponential term than that of eq. (15):

$$p_H \sim e^{-2\alpha q_0 \sin(\theta/2)\xi}, \qquad (16)$$

where ξ is the spatial thickness of the boundary. The force on the defect implied by this term is the analog of the Peierls force acting on a dislocation in a crystalline solid. In that case, the energy of the dislocation oscillates as a function of its position relative to the lattice so that it can glide only if a force of finite amplitude (the Peierls' force) acts on the defect. In the present context, this force can be interpreted as a pinning force acting on the grain boundary the depends on the relative location of the phase of the envelope of the defect relative to the underlying periodic variation of the order parameter. It vanishes when the thickness of the defect is much larger than the wavelength of the pattern.

Equations (15) and (16) are formally analogous in their exponential dependence on the extent of the defect. There is however an important difference: The extent of the defect diverges at a supercritical bifurcation, but remains finite in the subcritical bifurcation to a hexagonal phase [$\xi = 15\lambda_0/(8\sqrt{6}\pi g)$ for the equation considered here]. As a consequence, a pinning potential cannot be avoided in defect motion in a modulated phase of hexagonal symmetry. Pinning effects leading to glassy states have been observed in numerical calculations in the hexagonal phase of systems with competing interactions,[38] in cell dynamical calcula-

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tions of the model considered here,[37] in numerical simulations of this model leading to the formation in labyrinth patterns,[50] and also in grain boundary dynamics of colloidal crystals.[51] Both for subcritical bifurcations, and supercritical bifurcations with small but finite ϵ pinning effects will complicate the determination of the laws of motion of defects and hence of coarsening laws. In addition, effective growth rates will be expected to depend on temperature, as has been shown by Boyer and Viñals.[49]

In conclusion, there is now a fairly complete picture on the slow scale motion of dislocations, disclinations, and grain boundaries in lamellar and hexagonal mesophases. However, there is still no agreement on the resulting coarsening law in extended samples that contain, at least at early times, an ensemble of defects. Chief among the difficulties reported by many authors is the fact that different coarsening laws are obtained for different linear scales of the structure $l(t)$ (e.g., derived from an orientation correlation function, or from a defect density). This is in violation of a scale invariant description implicit in the power law dependence of $l(t)$, and is an issue that needs to be investigated further. It is possible that pinning effects, either because of finite ϵ, or because a hexagonal phase is being investigated, introduce non generic corrections to the motion of each defect, and complicate the interpretation of the results.

Acknowledgments

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Jorge Vinals was born in Barcelona, Spain, in 1959. He obtained his Ph. D. (1983) in Physics at the University of Barcelona. He joined the Supercomputer Computations Research Institute of Florida State University in 1989, and since 2004 he is a Professor of Physics and Canada Research Chair in Nonequililbrium Materials at McGill University in Montreal (Canada). His research addresses nonlinear phenomena and pattern formation in fluid systems, soft matter and materials science.