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On the kinetics of partially conserved order parameters: a possible mechanism for pattern formation

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Abstract. Local correlations between kinetic events of cation/vacancy ordering in framework structures lead to 'partial conservation' of the order parameter. Mixing non-conserved and conserved kinetic processes leads to a bifurcation behaviour with uniform states for mainly non-conserved order parameter and periodic pattern formation if more than 1 out of 12 steps is conserved. Possible correlations with experimental observations are discussed.

1. Introduction

Recent experimental studies have shown that the kinetic behaviour of cation ordering in framework structures is correctly described by kinetic order parameters Q which have the same structural meaning as their equilibrium equivalents. Furthermore, the driving force of the kinetic process was identified as being virtually identical, beside some non-local parameters, to the excess Gibbs free energy G of the thermodynamic phase transition. Typical examples are as follows.

(i) Vacancy ordering in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ where $Q = \langle s \rangle$ is the occupancy [1-3] of oxygen on two competing lattice sites and $H = \sum J_{ij} S_i S_j$; transient tweed patterns leading to stripe formation were found experimentally [4-7] and via computer simulation [8-12].

(ii) Al, Si ordering in Na feldspar where Q_{od} describes the degree of Al, Si ordering. Q_{od} 'slaves' another, structural order parameter Q (od = order disorder). The rate law is

$$Q_{\text{od}} = \frac{1}{\tau} \exp(\Delta G_a/kT) \partial G(Q_{\text{od}}, Q) / \partial Q_{\text{od}} \quad \text{with } \Delta G_a = \Delta G_a^0 + \epsilon Q^2$$

where G is the equilibrium excess Gibbs free energy of Q_{od} with relaxed Q . Transient tweed structures were observed [13].

(iii) Non-convergent ordering of Al and Si in K feldspar. The non-symmetry-breaking order parameter Q_t follows

$$Q_t = \frac{1}{\tau} \exp(\Delta G_a/kT) \partial G / \partial Q_t \quad \text{with } G = -H Q_t + \frac{1}{2} A (T - T_c) Q_t + \dots$$

No transient domain pattern was found [14].

(iv) Al, Mg ordering in omphacite, following

$$Q = \frac{1}{\tau} \exp(G_a/kT) \partial G / \partial Q \quad G_a = G_a^0 - \epsilon Q^2 \quad G = \frac{1}{2} \Delta (T - T_c) Q^2 + \frac{1}{6} C Q^6$$

with no transient domain pattern observed [15-16].

A similar connection between equilibrium behaviour and kinetic processes as in these ordering processes is also expected beyond the relaxational Landau-Khalatnikov behaviour

for displacive ferroelastics and ferroelectrics. The characteristic time scale in displacive systems is the phonon time scale which makes the experimental observation of transient states excessively difficult [17].

In the case of cation ordering in framework structures, it has been shown that the essential distinction between various rate behaviours is related to the smallest step that an order parameter (or the equivalent state variable) can make in order to reach equilibrium [18–21]. Two extreme cases have been well documented: firstly the Ising model in which the step size is $\delta Q = 1/N$, where N is the number of spins in the system. In this case the Glauber rate law for non-conserved order parameters and the Kawasaki rate law for conserved order parameters are applicable [22–30]. Secondly, in ferroelastic systems, the minimum step size is $\delta Q \ll 1/N$. This situation also holds for m -state Potts models ($m > 3$) [31]. In these cases, continuous rate laws of the type

$$\dot{Q} = \frac{1}{\tau} \left(1 - \frac{\xi_c^2 \sinh(\xi \nabla)}{\xi^2 \xi \nabla} \right) \frac{\partial G}{\partial Q} = -L(\Delta) \frac{\partial G}{\partial Q} \quad (1)$$

are a good approximation [8, 17, 31]. The new parameter introduced in this rate law is ξ_c which measures the importance of the order parameter conservation. The two limiting cases are easily identified. For $\xi_c = 0$ there is no conservation and we find a Landau–Khalatnikov form of rate equation (note, however, that the rate laws are supposed to describe essentially the full Q -dependence of the kinetic process even far from equilibrium whereas the Landau–Khalatnikov equation only describes relaxations of states close to equilibrium into the equilibrium state). We use here the term ‘Landau–Khalatnikov’ in a formal sense to indicate that the kinetic operator $L(\Delta)$ in (1) is simply the inverse time constant. For $\xi_c = \xi$ the order parameter is fully conserved and the rate law is in the lowest order of the Cahn–Hilliard type [32–35].

From a purely mathematical viewpoint it is clear that one cannot apply perturbation theory to describe the full range of $\xi_c > 0$ as a perturbation of $\xi_c = 0$ because the perturbation enters as a singular perturbation of derivatives higher than those contained in the starting equation. Here we are interested in the physical picture of the breakdown of the perturbation approach.

It is important for the following discussion to notice the different structure of the discrete and continuous rate laws as far as the conservation behaviour is concerned. Only in the case of the continuous rate law can the conservation behaviour be described by the kinetic operator $L(\Delta)$ with a continuous scaling between the fully conserved to the fully non-conserved limits. This paper is now concerned with the question: ‘What is the influence of small contributions of conservation to an essentially non-conserved rate behaviour?’

Before we discuss possible answers to this question, let us clarify the term ‘conservation’. Conserved order parameters generally describe processes such as chemical exsolution, spinodal decomposition etc. where the external constraint to the kinetic rate law is the invariance of the chemical composition. In other words, any change of the order parameter somewhere in the system has to be compensated by another change in the opposite direction somewhere else. In the language of Ising models, changes of the spin coordinate occur via flip–flop motion for conserved cases and via independent flip motions for non-conserved cases. The same behaviour holds for continuous order parameters: changes of the order parameter on a local scale can be correlated with changes in the opposite direction in another part of the crystal (flip–flop) if some degree of conservation exists. One sees clearly here the relative nature of such constraints: it is very likely that over small distances inside the crystal such correlated flip–flop behaviour is relevant, whereas over large distances such correlations die out. In these cases, the conservation behaviour is ‘partial’ and we wish to

explore what consequences such partial conservation has for the macroscopic rate behaviour [29,30].

In view of the importance of partially conserved kinetic behaviour for complex structures, such as many minerals and other materials encountered in earth sciences and material sciences, let us illustrate possible mechanisms with a typical example. Many framework structures, such as feldspars and cordierite, contain as structural units simple polyhedra which, in turn, consist of primitive simplexes such as tetrahedra. These are the smallest relevant units for structural phase transitions, kinetic processes and because of their relative rigidity with respect to deformation and relaxation, they are often called 'rigid units'. The analysis of structural phase transitions in terms of the response of these rigid units, i.e. the 'rigid unit modes' has been one of the most fruitful recent developments in the field of phase transitions [36–38]. Let us now consider a hexagonal framework of such tetrahedral rigid units, e.g. similar to the cordierite structure (figure 1) [39–40]. The essential process underlying the kinetics of Al, Si ordering in this structure is related to the distribution of Al in such a way that two Al positions occupy two opposite corners of each hexagon and also have the maximum distance between Al of different hexagons. The only way to achieve this distribution is within an orthorhombic or monoclinic system, whereas the disordered structure is hexagonal. In this example the smallest unit that is relevant for the kinetic process is one hexagon with three states for the maximum Al, Al distance, six states for distances with one Si between them and six states for neighbouring Al, Al arrangements. The smallest unit has, thus, fifteen states with three energy levels which split due to the coupling with the surrounding lattice. This scenario leads to a phase transition which has been described quantitatively in terms of Landau theory [41]. Let us now turn to the kinetic process. The great number of states [18, 19] and the coupling of the order parameter with the lattice strain lead to the applicability of mean-field theories [1] and the rate equation (1). If each of the elementary kinetic steps occurs independently, then the interaction with the mean field may drive the system into equilibrium via a non-conserved rate behaviour ($\xi_c = 0$). There are two obvious processes that may lead to strong correlations, however. The first is that each breaking of a chemical bond in one hexagon can trigger a similar bond breaking in the next hexagon within the constraints of the hexagonal matrix. This will lead to a reshuffle of the Al positions such that the change in one hexagon is compensated in another hexagon, so the total effect on the lattice is minimal. The second possible process is that the bond breaking leads to a separation of Al from the hexagon. In this case, Al goes into an interstitial site and diffuses through the structure. Recombination will occur with an empty site which is not further away than the diffusion length. If this site was also vacated by Al, nothing has changed. If, on the other hand, the site was vacated by Si, an effective change of order parameter has occurred via an exchange reaction. This exchange reaction is described by an order parameter flow with a conserved rate equation. This conserved process is in excess of the underlying non-conserved kinetic process with the same effective driving force. The total rate behaviour is partially conserved, therefore.

These two processes of correlated bond breaking and conserved exchange reactions (and possible other, yet unknown atomistic processes) lead to a mixture of conserved and non-conserved kinetics. Their driving force may be identical and the most simple rate equation describing such a scenario is given in (1).

We can now 'sharpen up' our original question and ask: 'Can we treat the additional correlations, i.e. the small admixtures of conservation, as a small perturbation of the otherwise non-conserved rate law?' It is the purpose of this paper to argue that the answer to this question is 'no'. It will be shown that perturbation theory breaks down even for rather small correlations which leads to a bifurcation between a regime with individual kink

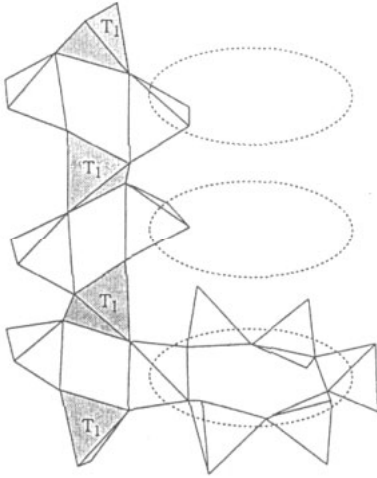


Figure 1. Sketch of the cordierite structure. The relevant kinetic ordering process relates to the distribution of two aluminium atoms over the six available tetrahedra positions per ring. The rings are interconnected via the T_1 tetrahedra. The orthorhombic ordering requires maximum Al-Al distances in each ring and translational symmetry between the rings (Courtesy A Putnis, Cambridge).

domains and oscillatory pattern formation.

2. The rate equation

The general rate law in (1) can be written for small values of ξ_c , i.e. close to the non-conserved limit, in lowest order and in an isotropic medium as [18]

$$\dot{Q} = -\frac{1}{\tau} \left(1 - \frac{1}{6} \xi_c^2 \Delta - \frac{1}{120} \xi_c^2 \xi^2 \Delta^2 \right) \partial G / \partial Q \quad \Delta = \nabla^2. \quad (2)$$

For the excess Gibbs free energy, a Landau expression is assumed

$$G = \frac{1}{2} A Q^2 + \frac{1}{4} B Q^4 + \frac{1}{2} g |\nabla Q|^2. \quad (3)$$

Using the total derivatives of the order parameter, we find

$$\dot{Q} = -\frac{1}{\tau} \left(1 - \frac{1}{6} \xi_c^2 \Delta - \frac{1}{120} \xi_c^2 \xi^2 \Delta^2 \right) (A Q + B Q^3 - g \Delta Q). \quad (4)$$

In anisotropic media the Laplace operators Δ have, in general, directional dependent prefactors because the 'easy direction' of the kink formation (last Laplacian) is not necessarily identical with the direction of maximum correlation (e.g. the 'easy' diffusion direction in the first Laplacian). These directional effects will be discussed in a separate paper. Here we project the spatial dependence of Q on a one-dimensional model with

$$\Delta = \partial^2 / \partial r^2. \quad (5)$$

Equation (4) is now renormalized with respect to the time variable

$$t' = t / (\tau |A|) \quad (6)$$

and the order parameter

$$\phi = Q / \sqrt{-A/B} \quad (A < 0) \quad (7)$$

leading to

$$\begin{aligned} \dot{\phi} = \phi - \phi^3 + (g/|A| - \frac{1}{6} \xi_c^2) \Delta \phi - \frac{1}{120} \xi_c^2 \xi^2 \Delta^2 \phi - (\frac{1}{6} \xi_c^2 g/|A|) \Delta^2 \phi \\ + \xi_c^2 \phi (\Delta \phi)^2 + \frac{1}{2} \xi_c^2 \phi^2 \Delta \phi. \end{aligned} \quad (8)$$

The term in the first bracket is the only prefactor that may change sign as a function of the control parameter. In ferroelastic framework structures, the thickness of a domain wall is, besides a factor of the order unity, $w = \sqrt{g/|A|} < 10 \text{ \AA}$ at $T \ll T_c$.

The characteristic length ξ_c represents the scaling length of the conservation and we focus first on the limit of $\xi_c < w$. In this case, the prefactor is $(w + (1/\sqrt{6})\xi_c)(w - (1/\sqrt{6})\xi_c) > 0$. Rescaling the length as

$$x = r/(w^2 - \frac{1}{6}\xi_c^2)^{1/2} \tag{9}$$

we find the rescaled rate equation

$$\dot{\phi}' = \phi - \phi^3 + \phi_{xx} - \gamma\phi_{xxxx} + \delta\phi_x^2 + \epsilon\phi^2\phi_{xx} \tag{10}$$

with

$$\gamma = [\frac{1}{6}w^2\xi_c^2/(w^2 - \frac{1}{6}\xi_c^2)^2] + \frac{1}{120}\xi_c^2\xi_c^2/(w^2 - \frac{1}{6}\xi_c^2)^2 > 0 \tag{11}$$

and

$$\delta = \xi_c^2/(w^2 - \xi_c^2) > 0 \quad \epsilon = \frac{1}{2}\xi_c^2/(w^2 - \xi_c^2) > 0 \quad \phi' = \frac{d}{dt'}\phi. \tag{12}$$

Close to a second-order phase transition, w diverges as $|T - T_c|^{1/2}$ and γ decays as $T_c - T$. The terms representing the partial conservation disappear at T_c and the conservation becomes thermodynamically irrelevant. At $T \ll T_c$, we estimate $w = 10 \text{ \AA}$, $(1/\sqrt{6})\xi_c = 5 \text{ \AA}$, and $\gamma = \frac{1}{4}$. The expected numerical values of γ are for these length scales between zero at T_c and $\frac{1}{4}$ at low temperatures. The maximal values of δ and ϵ are, using the same estimates, 2 and 1, respectively.

3. Analytical solutions and marginal stabilities

The limiting case $\gamma = \epsilon = \delta = 0$ has a relevant solution for boundary conditions $\phi = 1$ at $x = \infty$ and $\phi = -1$ at $x = -\infty$ kinks ($\phi = \tanh x$) representing twin boundaries [42-46]. The growth of the stable state $\phi = 1$ into matrix of unstable $\phi = 0$ material under isothermal conditions is also described by kinks. Their velocity is determined by the marginal stability of the progressing front with respect to fluctuations [47-52]. This marginal velocity is $v^* = 2$ for (10). In units of the Landau potential, $v = (2/\tau)(-gA)^{1/2}$ which decay with exponent $\frac{1}{2}$ for $T \rightarrow T_c$.

For small values of γ , this situation will not change (note $\phi = 0$ at the leading edge of the propagating wavefront). The dispersion is identical with that of the well-studied extended Fisher-Kolmogorov (EFK) equation [53-54] namely

$$\text{Re}(\omega) = 1 + k_r^2 - k_i^2 - \gamma(k_r^4 - 6k_i^2k_r^2 + k_i^4) \tag{13}$$

where $k_r = \text{Re}(k)$ and $k_i = \text{Im}(k)$.

The maximum growth rate is determined by the maximum of $\text{Re}(\omega)$ with respect to k_i at $k_r = k_r^*$ for marginal stability of the wavefront. For $\gamma < \frac{1}{12}$, one finds $k_i = 0$, so only individual kinks will propagate. In this case, the partial conservation does change the effective parameters of the kinetic equation but does not modify the essential physical behaviour. This situation changes dramatically when γ approaches $\frac{1}{12}$ and increases further. For $\gamma > \frac{1}{12}$, the individual kinks are replaced by nearly periodic kink-antikink pattern (figure 2). Their repetition length λ is approximately

$$\lambda = (8\pi/3)(2\gamma/A)^{1/2}(2 + 24\gamma - A)/[12(\gamma - \frac{1}{12}) - A] \tag{14}$$

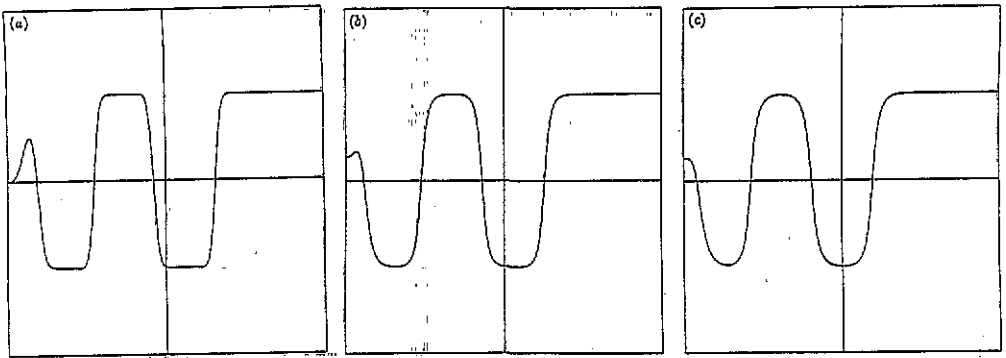


Figure 2. Snapshots of a moving wavefront (from right to left). On the RHS the initial condition is the uniform state with the equilibrium order parameter Q_{eq} . This phase grows into the unstable phase with $Q = 0$ via pattern formation. The growth is described by (10) with (a) $\gamma = 0.3$ and $\delta = \epsilon = 0$, (b) $\delta = 1.5$, $\epsilon = 3$ and (c) $\delta = 3$, $\epsilon = 6$. The increase of δ and ϵ leads to a rounding of edges but has little influence on the general pattern formation.

where

$$A = (7 + 24\gamma)^{1/2} - 3. \quad (15)$$

The repetition length diverges at the bifurcation point [53] as

$$\lambda \propto \left(\gamma - \frac{1}{12}\right)^{-3/2}. \quad (16)$$

At $\gamma \gg \frac{1}{12}$, the repetition length depends only weakly on the numerical value of γ with $\lambda = 250 \text{ \AA}$ at $\gamma = \frac{1}{2}$ and the parameters estimated as given before.

At this point we notice that the transient state produced similar periodic patterns for a large number of functions $\partial G(\phi)/\partial \phi$ [55]. In the case considered above, a sample was quenched from $\phi = 0$ to $\phi = 1$. Experimentally, a similar pattern also evokes for shock heating from $\phi = 1$ to $\phi < 1$, although a direct comparison with experiment is difficult because we have so far ignored the directional dependences of the prefactors of the two Δ -operators. A particular effect in ferroelastic materials is that one finds two orthogonal propagation directions and, consequently, the formation of tweed pattern rather than periodic twins. In figure 3 two typical examples are shown. A crystal of Na feldspar was shock heated and the tweed microstructure shown in figure 3(a) with $\lambda \simeq 200 \text{ \AA}$ occurs for all intermediate times ($0.2 < Q < 0.8$). In figure 3(b) the similar pattern for quenched Mg cordierite is shown. In both examples, the pattern formation is due to Al, Si ordering.

4. Cases with ξ_c similar to and larger than w

So far the discussion has been concerned with the limiting case of very weak conservation. For cases where ξ is still so small that the series expansion of $\sinh(\xi k)/\xi k$ is a good approximation one can expect many conserved steps to occur inside the conservation volume defined by ξ_c . In this case the condition $w > \xi_c$ is no longer fulfilled. The sign of the first Laplacian then changes to negative or the term disappears for $w = (1/\sqrt{6})\xi_c$.

In this special case [56–57] the propagating wavefront follows

$$\phi'_t = \phi - \phi^3 - \gamma^* \phi_{xxxx} + \delta^* \phi \phi_x^2 + \epsilon^* \phi_{xx}^2 \quad (17)$$

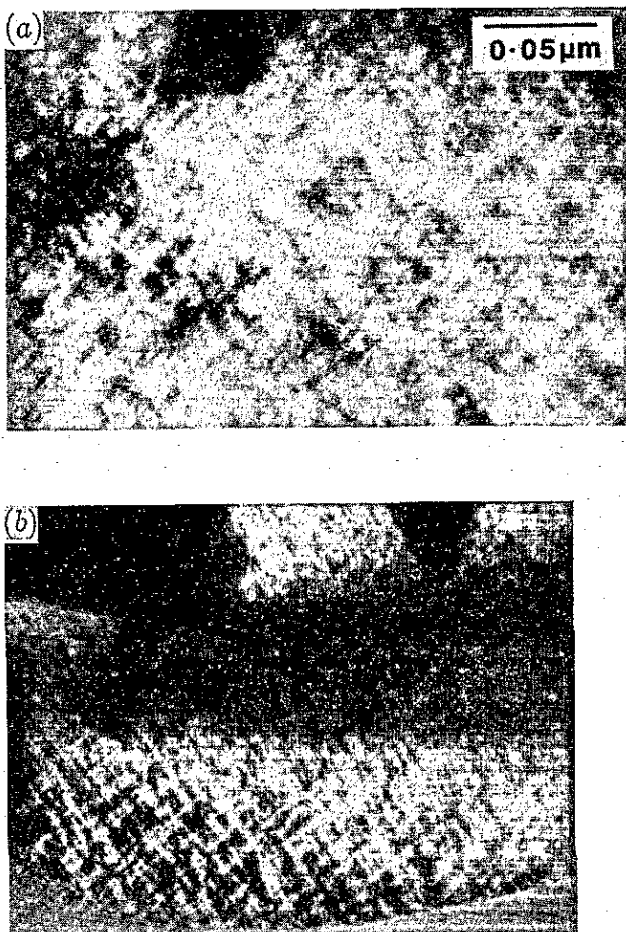


Figure 3. Tweed microstructures as transient patterns during the course of a kinetic cation (dis)ordering experiment: (a) Na feldspar, Al, Si disordering, (b) cordierite, Al, Si ordering. (Courtesy A Putnis, Cambridge.)

with

$$\gamma^* = \frac{1}{6}\xi_c^2\omega^2 + \frac{1}{120}\xi_c^2\xi^2 \quad \delta^* = \xi_c^2 \quad \epsilon^* = \frac{1}{2}\xi_c^2. \quad (18)$$

Equation (17) is similar to those describing propagation of instabilities in the direction parallel to the long roll axis in Rayleigh-Bénard cells. These fronts also produce kinks so that the microstructure consists again of a kink-antikink pattern.

The non-singular case of a negative term in the second order spatial derivative is similar to the dynamics transient pattern formation in liquid crystals, e.g. the Fréedericksz, instability [58]. In order to illustrate the close connection, let us start from the kinetic equation to the field $\phi(r) = [n(r), v(r), u(r)]$ where n is the usual director field, v is the velocity and u describes the position of the molecules. The kinetic equation is written as

$$\phi_{t,i} = L_{ij}(\phi) \partial G / \partial \phi_j + \eta_i \quad i = 1, \dots, 9. \quad (19)$$

The last term is Langevin noise and L_{ij} is the kinetic operator. In nematic liquid crystals, the kinetic operator does not only describe the dissipation of the order parameters but also the non-dissipative coupling between the components of ϕ . The diagonal terms are

dissipative, the non-diagonal terms describe the coupling between several order parameters. The equivalence to the partial conservation in the original equation (1) is now introduced via the non-diagonal coupling terms, whereas the uncoupled equations would not describe the pattern formation at all. Translating this phenomenon into the language of structural phase transitions, it means that the local kinetic correlations, which are essential for the partial conservation, are not necessarily brought about by a mechanism which is related to the driving order parameter itself, but is due (in this model) to the coupling to another degree of freedom which, *per se*, is not involved in the mechanism of the equilibrium phase transition.

It has been shown that the kinetic equation (19) can be diagonalized in terms of the angular dependence of n only:

$$n_x(x, z) = \cos(\phi)(x, z) \quad n_y(x, z) = \sin(\phi)(x, z) \quad n_z = 0. \quad (20)$$

Transforming ϕ into Fourier space, with the amplitude $\theta_{q_x}(t)$, the equivalent kinetic equation of $\theta_{q_x}(t)$ is in lowest order

$$\dot{\theta}_{q_x}(t) = (1/\gamma) \left[a - bq_x^2 \right] \theta_{q_x}(t) + \eta_{q_x}(t). \quad (21)$$

The structure factor with anchoring boundary conditions in lowest order is

$$S_{q_x} = \langle \theta_{q_x}(t), \theta_{-q_x}(t) \rangle \quad (22)$$

with the time dependence

$$\dot{S}_{q_x} = (2/\bar{\gamma}) \left[a - bq_x^2 \right] S_{q_x}(t) + (4/\gamma) k_B T / V. \quad (23)$$

The kinetic prefactor depends itself on the wavevector via

$$\bar{\gamma} = \gamma - c / (\eta_c - \eta_a Q^{-2}) \quad Q = q_x / q_x^0 \quad (24)$$

which leads for realistic values of the viscosity parameters and early stages of the rate equation (12) with small Q -values to

$$1/\bar{\gamma} \simeq (1/\gamma) (1 - cQ^2/\gamma\eta_a) = L(Q). \quad (25)$$

The results for strong magnetic fields h (i.e. quenching deep into the low-symmetry phase) have been analysed numerically [60]. It was found that the uniform state for the initial conditions decays after the mean first passage time into a pattern with a well defined wavevector close to the maximum of the dispersion relation.

So far we have considered the pattern formation. As transient states, these patterns disappear when the system approaches equilibrium. The main question now concerns the decay channels for the pattern destruction. In case of fully conserved order parameters, this problem relates to coarsening. For non-conserved order parameters the destruction of twin boundaries is essentially due to the formation of junctions between walls and the pulling back of needle-shaped domains [42]. It appears that the driving mechanism for the destruction of tweed pattern is also the bending of domain walls around junctions and the subsequent retraction of bend walls (e.g. as needle tips) [42]. None of these atomistic processes is readily described by the 1D kinetic rate equations discussed so far. For $\xi_c < w$, the pattern appears to be numerically stable although exponentially small wall-wall interactions lead to the formation of ripple states [53, 61].

The more straightforward pattern with $\xi_c < w$ has been shown to be unstable with logarithmic increase of the $\langle \lambda \rangle \propto \ln t$ mean value of the repetition length [59, 62, 63]. This decay lay is dependent on long-distance exponential interaction between walls. Such interactions are shown to exist dynamically between Fréedericksz walls [51], and their existence is also generally assumed for structural twin walls [52] although their physical origin is less than clear.

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