

# Triblock Copolymer Theory: Ordered ABC Lamellar Phase

Xiaofeng Ren

Department of Mathematics and Statistics  
Utah State University  
Logan, UT 84322-3900, USA

Juncheng Wei \*

Department of Mathematics  
Chinese University of Hong Kong  
Shatin, Hong Kong

December 2, 2002

## Abstract

The *ABC* lamellar phase of a triblock copolymer in the strong segregation region is studied on periodic and bounded intervals. In the periodic case we find a family of local minimizers of the free energy functional all with a fine lamellar structure. Among these local minimizers we identify the one most favored by the free energy, and hence determine the thickness of lamellar microdomains. In the bounded interval case we show that perfect lamellar structure does not exist due to the boundary effect. We view the strong segregation limit as a  $\Gamma$ -limit of the free energy by a proper choice of the material sample size. The key step is the spectral analysis of a large matrix resulted from the second derivative of the  $\Gamma$ -limit.

Key words. triblock copolymer, local minimizer, global minimizer,  $\Gamma$ -convergence  
2000 Mathematics Subject Classification. 34D15, 45J05, 82D60

## 1 Introduction

Many important physical systems exhibit self-organization and pattern formation. One explanation for this phenomenon is the long-range interaction of Coulomb type (Muratov [34]). Examples include weakly charged polyelectrolyte solutions (Erukhimovich and Khokhlov [13], Borue and Erukhimovich [3], Nyrkova, Khokhlov and Doi [37]), cross linked polymer mixtures (de Gennes [10]), amphiphile solutions (Stillinger [49]), phase-separating ceramic compounds (Chen and Khachaturyan [7]), photostimulated phase transitions (Mamin [28]). A number of quantum systems such as degenerate magnetic semiconductors and high-temperature superconductors which exhibit electronic phase separation can be considered as systems with competing Coulomb interactions (Emery and Kivelson [12]). In addition the general problem of Wigner crystallization (Care and March [5]) and the thermodynamic and glassy properties of spin systems frustrated by Coulomb interaction [12] can also be studied from this viewpoint. Here we study pattern formation in triblock copolymers.

Block copolymers belong to a class of soft materials that in contrast to crystalline solids, are characterized by fluid-like disorder on the molecular scale and a high degree of order at longer length scales. They are produced by joining two or more chemically distinct homopolymer blocks, each a

---

\*Supported in part by a Direct Grant from CUHK and an Earmarked Grant of RGC of Hong Kong.

linear series of identical monomers. The unlike monomers in the coil-like long chain molecules are thermodynamically incompatible. This results in microphase separation of monomer blocks on the molecular scale (5-100 nm) at low temperature, producing complex morphology phases.

In a diblock copolymer a molecule is a chain of  $A$  monomer units linked chemically to a chain of  $B$  monomer units. For instance in the isoprene-styrene diblock copolymer,  $A =$  isoprene and  $B =$  styrene. In a triblock copolymer, such as isoprene-styrene-2vinylpyridine (Mogi et al [32]), a molecule is a chain of  $A$  monomers, connected to a chain of  $B$  monomers, which is again connected to a chain of the third type  $C$  monomers. Triblock copolymers are new and, to the authors' knowledge, industrial applications are yet to be found, although experimental studies have been done [32].

The monomer density fields of block copolymers are identified as the macroscopic quantities that describe the morphology structures, and in turn determine many other physical properties. The formation and evolution of these densities make up the central part of the block copolymer theory. The reader may find more information in Bates and Fredrickson [2] on this exciting subject.

Here we are concerned with triblock copolymers. At high temperature a triblock copolymer is in a disordered phase. The monomer density fields are homogeneous (Ren and Wei [45]). If the temperature is lowered, the triblock copolymer undergoes a phase transition. Higher symmetry of the disordered phase gives way to lower symmetries of ordered phases.

Three parameters  $\chi^{AB}N$ ,  $\chi^{BC}N$  and  $\chi^{CA}N$  are responsible for phase transitions. The three  $\chi$ 's are called the Flory-Huggins parameters, defined in (3.15), and are inversely proportional to temperature.  $N$ , the polymerization index, is the number of all the monomers in a chain molecule. When  $\chi^{AB}N$ ,  $\chi^{BC}N$  and  $\chi^{CA}N$  increase, achieved by having low temperature or large  $N$ , the disordered homogeneous phase of the block copolymer becomes unstable. Inhomogeneity of monomers appear and one observes microdomains rich in one of the three monomer types. It is shown in [45] that immediately after the disordered phase becomes unstable, the sizes of the microdomains are of order  $N^{1/2}$ . This state of microdomain separation is called weak segregation.

If one further increases  $\chi^{AB}N$ ,  $\chi^{BC}N$  and  $\chi^{CA}N$ , the microdomains grow to sizes of order  $N^{2/3}$ , a phenomenon called strong segregation. In this region there exist many ordered phases, known as morphology phases [2]. Here we study the lamellar phase. Combining with the results in [45] we will have a theory that explains disorder to lamellar phase transition in triblock copolymers.

The main result here is the existence of the  $ABC$  lamellar phase in the strong segregation region, presented in Section 4, as a local minimizer of the free energy functional  $I_\varepsilon$ , defined in (2.9), in 1-dimension with the cyclic  $ABC$  pattern and the periodic boundary condition.

To prove this result we first show in Section 3 that the strong segregation limit is indeed the  $\Gamma$ -limit,  $J$  defined in (3.16), of the singular perturbation theory, if we choose the size of the sample properly. In the  $\Gamma$ -limit we find a  $ABC$  lamellar local minimizer of  $J$  on the periodic domain  $\mathbf{R}/\mathbf{Z}$ . It perturbs to become a local minimizer of  $I_\varepsilon$  for small  $\varepsilon$ . It is easy to find a lamellar structure as a critical point of  $J$ , but far more difficult is to prove that it is indeed a nondegenerate local minimizer. For this we study the spectrum of the second derivative of  $J$ . This is done in Section 5 where we use a "coarse" Fourier transform to find some 3-dimensional invariant subspaces, in which we study eigenvalues. The procedure is complex for several reasons. First we are dealing with a vector valued problem. Second the nonlinear function  $J$  is not explicit enough. And third we do not know a priori the number of microdomains (or interfaces). We set this number to be a variable  $3\nu$  of arbitrary size.  $J$  has  $3\nu - 2$  degrees of freedom. We prove the existence of a  $ABC$  lamellar phase for each  $\nu$ . We also minimize the reduced free energy  $J$  among this family of local minimizers to find the one particular lamellar phase most favored by  $J$  and also  $I_\varepsilon$ .

In Section 6 we consider  $I_\varepsilon$  on the interval  $(0, 1)$ . The strong segregation limit is again a  $\Gamma$ -limit.

However in this case due to the boundary effect we no longer have a perfect lamellar phase. We illustrate this point by constructing some local minimizers. Numerical calculation suggests that local minimizers with cyclic patterns tend to have lower energies compared to the ones with non-cyclic patterns. But cyclic local minimizers never have fine periodicity. On the other hand there exist some peculiar non-cyclic local minimizers with perfect “anti-symmetry”.

There have been few mathematical studies other than [45] on triblock copolymers to this day. On the mathematical aspects of diblock copolymers we refer to Nishiura and Ohnishi [36], Ohnishi, et al [38], Ren and Wei [42, 41, 43, 44], Fife and Hilhorst [15], Choksi [9], and Henry [23]. The results obtained here are the vector versions of some of the results in [42] for the scalar diblock copolymer problem.

## 2 The free energy functional

A density functional theory for triblock copolymers was first derived in Nakazawa and Ohta [35]. The model we use here is taken from a mathematically more rigorous work by the authors [45]. There are three main steps in the derivation. The original system has a picture of interacting chain molecules. It is a complex problem of equilibrium statistical physics. In the second step one uses the idea of mean fields to express the free energy of the system as a functional of the effective mean potential fields (Helfand [19], Helfand and Wasserman [20, 21, 22], Hong and Noolandi [24, 25], Matsen and Schick [29]). This theory is called the self-consistent field theory. The monomer density fields may also be expressed as functions of the mean fields. In the third step one reverses the dependence of the monomer density fields on the mean fields to express the free energy as a functional of the density fields (See Leibler [27], Ohta and Kawasaki [39] for this idea applied to diblock copolymers).

Suppose that in a triblock copolymer molecule there are  $N_A$  type  $A$ ,  $N_B$  type  $B$ , and  $N_C$  type  $C$  monomers. The Kuhn statistical length [11, 18] measures the average length between two adjacent monomers in a chain. We assume that this length is independent of the types of adjacent monomers, and denote it by  $l$ . The relative numbers of the three type monomers in every molecule are

$$a = \frac{N_A}{N} > 0, \quad b = \frac{N_B}{N} > 0, \quad c = \frac{N_C}{N} > 0, \quad (a + b + c = 1)$$

where  $N = N_A + N_B + N_C$  is the polymerization index, a large number at least in the thousands. The triblock copolymer is made of identical chain molecules just described, and is confined in a container  $\Omega$  whose volume is  $|\Omega|$ . If the monomer densities at every  $y \in \Omega$  are  $\rho(y) = (\rho_A(y), \rho_B(y), \rho_C(y))$ , the free energy  $F$  can be expressed in terms of  $\rho$ .

The average number of monomers of all three types per unit volume is denoted by  $\rho_0$ . Temperature is measured in the energy unit so the Boltzmann constant is 1 and  $\beta$  is the inverse of the absolute temperature. To separate the size effect of  $\Omega$  from the shape effect of  $\Omega$ , we scale  $\Omega$  to  $D = \{x : |\Omega|^{1/3}x \in \Omega\}$  of unit 3-dimensional Lebesgue measure. Introduce relative densities  $u_k(x) = \rho_k(|\Omega|^{1/3}x)/\rho_0$ , and let  $u = (u_A, u_B, u_C)^T$  and  $\bar{u} = (\bar{u}_A, \bar{u}_B, \bar{u}_C)^T$ , where  $\bar{u}_k := \int_D u_k(x) dx$  denotes the average of  $u_k$ . The superscript  $T$  denotes the transpose of a vector. The free energy model deduced in [45] is the dimensionless  $I = \beta F/(\rho_0|\Omega|)$ , the relative free energy per monomer, as a functional of the order parameter  $u$ :

$$I(u) = \int_D \left[ \frac{\epsilon^2}{2} \nabla u \cdot \nabla u + \frac{\sigma}{2} (-\Delta)^{-\frac{1}{2}}(u - \bar{u}) \cdot (-\Delta)^{-\frac{1}{2}}(u - \bar{u}) + W(u) \right] dx. \quad (2.1)$$

The coefficient  $\epsilon^2$  is a diagonal matrix.  $\epsilon^2$  is written as a square for notation consistency with the diblock copolymer problem [42, 41]. The second coefficient  $\sigma$  is a symmetric matrix. The entries of the two matrices are

$$(\epsilon^2)^k := (\epsilon^2)^{kk} = \frac{l^2}{6|\Omega|^{2/3}} K^{kk}, \quad \sigma^{km} = \frac{6|\Omega|^{2/3}}{l^2 N^2} L^{km}, \quad (2.2)$$

where the matrices  $K$  and  $L$  are

$$K = \frac{1}{2} \begin{bmatrix} \frac{1}{a} & 0 & 0 \\ 0 & \frac{1}{b} & 0 \\ 0 & 0 & \frac{1}{c} \end{bmatrix}, \quad L = \frac{3}{2(ab + bc + ca)} \begin{bmatrix} \frac{b+c}{a^2} & -\frac{c}{ab} & -\frac{b}{ca} \\ -\frac{c}{ab} & \frac{c+a}{b^2} & -\frac{a}{bc} \\ -\frac{a}{ca} & -\frac{a}{bc} & \frac{a+b}{c^2} \end{bmatrix}. \quad (2.3)$$

The first and second terms in (2.1) are written in the matrix form, i.e.

$$\epsilon^2 \nabla u \cdot \nabla u = \sum_k (\epsilon^2)^k |\nabla u_k|^2,$$

$$\sigma (-\Delta)^{-\frac{1}{2}} (u - \bar{u}) \cdot (-\Delta)^{-\frac{1}{2}} (u - \bar{u}) = \sum_{k,m} \sigma^{km} (-\Delta)^{-\frac{1}{2}} (u_k - \bar{u}_k) (-\Delta)^{-\frac{1}{2}} (u_m - \bar{u}_m).$$

They form the entropy part of the free energy. The third integrand comes from the internal energy, which is initially defined to be

$$W(u) = \sum_{k,m} \frac{\beta V^{km}}{2} u_k u_m. \quad (2.4)$$

$V^{km}$  is the interaction energy between a  $k$  monomer and an  $l$  monomer.  $V^{km} = V^{mk}$  and  $V^{km} > 0$  for any  $k, m \in \{A, B, C\}$ .

The nonlocal operator  $(-\Delta)^{-1/2}$  is the square root of the inverse of the negative Laplace operator. Its exact definition must be compatible with the admissible set of  $I$ . The integrand in  $I$  is therefore a nonlocal constitutive relation between the order parameter  $u$  and the free energy density field. For this reason  $I$  is called a nonlocal variational problem. One may rewrite the nonlocal part of  $I$  as

$$\int_D \frac{\sigma}{2} (u - \bar{u}) \cdot (-\Delta)^{-1} (u - \bar{u}) dx,$$

where  $(-\Delta)^{-1}$  is really the Green function of  $-\Delta$  with the Neumann boundary condition. The Green function splits into the fundamental solution part and the regular part. The fundamental solution is  $\frac{1}{4\pi|x-y|}$  in space, which is the Coulomb potential. This is why we say in the introduction that the nonlocal interaction is of Coulomb type.

Since the total number of  $A$  ( $B$  and  $C$  respectively) monomers in  $\Omega$  is  $a\rho_0|\Omega|$  ( $b\rho_0|\Omega|$  and  $c\rho_0|\Omega|$  respectively), we have the monomer number constraints

$$\bar{u}_A = a, \quad \bar{u}_B = b, \quad \bar{u}_C = c. \quad (2.5)$$

We also assume that the material is incompressible, i.e.  $\rho_A(y) + \rho_B(y) + \rho_C(y) = \rho_0 \quad \forall y \in \Omega$ , or

$$u_A(x) + u_B(x) + u_C(x) = 1, \quad \forall x \in D. \quad (2.6)$$

Under this constraint the  $W$  term in (2.1) is (2.4) if  $0 \leq u_A, u_B, u_C \leq 1$  and  $u_A + u_B + u_C = 1$ , and  $W(u) = \infty$  otherwise. On  $0 \leq u_k \leq 1$  and  $u_A + u_B + u_C = 1$ ,  $W$  is typically concave (but not always so, see Section 7) and there exist three local minima at the corners  $(1, 0, 0)$ ,  $(0, 1, 0)$  and  $(0, 0, 1)$ . To make the problem more mathematically tractable, a linear term

$$W(1, 0, 0)u_A + W(0, 1, 0)u_B + W(0, 0, 1)u_C = \sum_k \frac{\beta V^{kk}}{2} u_k \quad (2.7)$$

is subtracted from the original  $W$ . This only changes  $I$  of (2.1) by a constant  $\sum_k \frac{\beta V^{kk}}{2} \bar{u}_k$ , not affecting any minimization operation on  $I$ . The new  $W$  is  $\geq 0$  and  $W(z) = 0$  if and only if  $z = (1, 0, 0)^T$ ,  $(0, 1, 0)^T$ , or  $(0, 0, 1)^T$ . We also change the discontinuous feature of  $W$ .

In summary  $W$  is a smooth function defined on the plane

$$P = \{(z_A, z_B, z_C)^T \in \mathbf{R}^3 : z_A + z_B + z_C = 1\}$$

so that  $W(z) \geq 0$  for every  $z \in P$ .  $W(z) = 0$  exactly when  $z = (1, 0, 0)^T$ ,  $(0, 1, 0)^T$ , or  $(0, 0, 1)^T$ . For technical simplicity we assume that as  $|z| \rightarrow \infty$ ,  $W(z) \rightarrow \infty$  quadratically.

**Remark 2.1** *It also makes sense to remove the incompressibility condition (2.6) and consider a compressible triblock copolymer. Then we would extend the domain of  $W$  to  $\mathbf{R}^3$  so that  $W(z) \geq 0$  and  $W(z) = 0$  if and only if  $z = (1, 0, 0)^T$ ,  $(0, 1, 0)^T$ , or  $(0, 0, 1)^T$ .*

Since we are only interested in the lamellar phase of the triblock copolymer in this paper, we take the domain  $\Omega$  to be  $(0, d)^3$  so  $|\Omega|^{1/3} = d$  and  $D = (0, 1)^3$ . Introduce

$$\varepsilon = \frac{l}{\sqrt{6}d}, \quad \gamma = \frac{6\sqrt{6}d^3}{l^3 N^2}, \quad (2.8)$$

so that by (2.2)

$$\epsilon^2 = \varepsilon^2 K, \quad \sigma = \varepsilon \gamma L.$$

We choose the size of  $\Omega$  in a rather special way so that  $d \sim N^{2/3}l$ . As a consequence  $\gamma \sim 1$  is a fixed positive constant. This choice of  $d$  will later facilitate the use of the  $\Gamma$ -convergence theory, from which follow the existence of the lamellar phase and the estimate of the microdomain size. Regarding  $\varepsilon$  we assume that  $\varepsilon \rightarrow 0$ , a consequence of  $d \sim N^{2/3}l$  and  $N \rightarrow \infty$ . This puts the triblock copolymer in the strong segregation region.

In the lamellar phase the order parameter  $u$  depends on one space direction  $x \in (0, 1)$  only, so (2.1) becomes a family of functionals parameterized by  $\varepsilon$  in one space dimension:

$$I_\varepsilon(u) = \int_0^1 \left[ \frac{\varepsilon^2}{2} K u' \cdot u' + \frac{\varepsilon \gamma}{2} L(-\Delta)^{-\frac{1}{2}}(u - \bar{u}) \cdot (-\Delta)^{-\frac{1}{2}}(u - \bar{u}) + W(u) \right] dx. \quad (2.9)$$

Lacking better notation we continue to use  $\Delta$  to denote the second derivative.

We minimize  $I_\varepsilon$  locally in two admissible sets. The first one is

$$X := \{(u_A, u_B, u_C)^T : u_A, u_B, u_C \in W^{1,2}(0, 1) \text{ satisfy (2.5), (2.6)}\}. \quad (2.10)$$

In  $X$  the nonlocal operator is defined from the Laplace operator

$$\Delta : \{v \in W^{2,2}(0, 1) : v'(0) = v'(1) = 0, \bar{v} = 0\} \rightarrow \{u \in L^2(\Omega) : \bar{u} = 0\}.$$

Local minimizers of  $I_\varepsilon$  in  $X$  satisfy the Neumann boundary condition  $u'(0) = u'(1) = (0, 0, 0)^T$ . For technical reasons, we trivially extend the domain of  $I_\varepsilon$  from  $X$  to

$$\hat{X} = \{(u_A, u_B, u_C)^T : u_A, u_B, u_C \in L^2(0, 1) \text{ satisfy (2.5), (2.6)}\} \quad (2.11)$$

by setting  $I_\varepsilon(u) = \infty$  if  $u \in \hat{X} \setminus X$ . The  $L^2$  norm is used in  $\hat{X}$  to define its metric, i.e. for  $u_1, u_2 \in \hat{X}$  their distance is

$$\|u_1 - u_2\| = \left( \sum_{k=A,B,C} \|u_{1,k} - u_{2,k}\|_{L^2(0,1)}^2 \right)^{1/2}.$$

We also study the situation where the two end points 0 and 1 of  $D = (0, 1)$  are identified. Functions on this domain are treated either as 1-periodic functions on  $\mathbf{R}$ , or functions on the quotient space  $\mathbf{R}/\mathbf{Z}$ , which may be identified with a circle. So we have the second admissible set

$$Y := \{(u_A, u_B, u_C)^T : u_A, u_B, u_C \in W^{1,2}(\mathbf{R}/\mathbf{Z}) \text{ satisfy (2.5), (2.6)}\}. \quad (2.12)$$

Local minimizers of  $I_\varepsilon$  in  $Y$  satisfy the periodic boundary condition  $u(0) = u(1)$  and  $u'(0) = u'(1)$ . In  $Y$  the nonlocal operator is derived from

$$\Delta : \{v \in W^{2,2}(\mathbf{R}/\mathbf{Z}) : \bar{v} = 0\} \rightarrow \{u \in L^2(\mathbf{R}/\mathbf{Z}) : \bar{u} = 0\}.$$

Similarly we extend the domain of  $I_\varepsilon$  from  $Y$  to

$$\hat{Y} := \{(u_A, u_B, u_C)^T : u_A, u_B, u_C \in L^2(\mathbf{R}/\mathbf{Z}) \text{ satisfy (2.5), (2.6)}\} \quad (2.13)$$

by setting  $I_\varepsilon(u) = \infty$  if  $u \in \hat{Y} \setminus Y$  and with the  $L^2$  norm being the underline metric.

**Remark 2.2** In  $\hat{Y}$ ,  $I_\varepsilon$  is invariant under the translation group  $\mathbf{R}/\mathbf{Z}$ :  $u(\cdot) \in \hat{Y} \rightarrow u(\cdot - y) \in \hat{Y}, \forall y \in \mathbf{R}/\mathbf{Z}$ . Results concerning  $I_\varepsilon$  in  $\hat{Y}$  are often stated with phrases “up to translation” and “modulo translation”, to reflect this invariance.

### 3 $\Gamma$ -convergence

We show that as  $\varepsilon \rightarrow 0$ ,  $\varepsilon^{-1}I_\varepsilon$  converges to a singular limit  $J$ , the  $\Gamma$ -limit. First we need some definitions.

**Definition 3.1**  $X_0$  is the subset of  $\hat{X}$  such that  $u \in \hat{X}$  if  $u(x) = (1, 0, 0)^T, (0, 1, 0)^T$  or  $(0, 0, 1)^T$  for a.e.  $x \in (0, 1)$ , and each component of  $u$  is a function of bounded variation.

**Definition 3.2**  $Y_0$  is the subset of  $\hat{Y}$  such that  $u \in \hat{Y}$  if  $u(x) = (1, 0, 0)^T, (0, 1, 0)^T$  or  $(0, 0, 1)^T$  for a.e.  $x \in \mathbf{R}/\mathbf{Z}$ , and each component of  $u$  is a function of bounded variation.

The members in  $X_0$  ( $Y_0$  respectively) are vector-valued step functions, of finitely many jumps in  $(0, 1)$  ( $\mathbf{R}/\mathbf{Z}$  respectively). An  $AB$  interface is modeled by a jump discontinuity from  $(1, 0, 0)^T$  to  $(0, 1, 0)^T$ , (and similar discontinuities characterize  $BC$  and  $CA$  interfaces).

**Definition 3.3** For each  $AB$  interface the surface tension  $e^{AB}$  is

$$e^{AB} = \inf \left\{ \sqrt{2} \int_0^1 \sqrt{W(\eta(t))(K\eta'(t) \cdot \eta'(t))} dt : \eta \in \Lambda_{AB} \right\}$$

where  $\Lambda_{AB} = \{\eta \in C^1([0, 1], P) : \eta(0) = (1, 0, 0)^T, \eta(1) = (0, 1, 0)^T\}$ . Similarly define  $e^{BC}$  and  $e^{CA}$  to be surface tensions of  $BC$  and  $CA$  interfaces.

If we wish to interpret  $e^{AB}$  in terms of  $\beta V^{km}$  in (2.4), the constraint that  $\eta(t)$  is in the plane  $P$  implies that the  $\eta(t)$  that yields the infimum in Definition 3.3 is  $\eta(t) = (1, 0, 0)^T(1-t) + (0, 1, 0)^T t$ . The function  $W$  we use is, according to (2.4) and (2.7),

$$W(u) = \sum_{k,m} \frac{\beta V^{km}}{2} u_k u_m - \sum_k \frac{\beta V^{kk}}{2} u_k.$$

From these  $\eta$  and  $W$  we deduce

$$e^{AB} = \left( \int_0^1 \sqrt{(1-t)t} dt \right) \sqrt{\chi^{AB} \left( \frac{1}{a} + \frac{1}{b} \right)} = \frac{\pi}{8} \sqrt{\chi^{AB} \left( \frac{1}{a} + \frac{1}{b} \right)}, \quad (3.14)$$

and similar expressions for  $e^{BC}$  and  $e^{CA}$ . The constants  $\chi^{km}$  in  $e^{km}$  are called the Flory-Huggins parameters [11, 18] in polymer science and are defined by

$$\chi^{km} = \beta V^{km} - (\beta/2)(V^{kk} + V^{mm}) > 0, \quad k \neq m. \quad (3.15)$$

The three parameters are all positive, because in a block copolymer, unlike monomers repel each other more than like ones do. Note that our problem depends on  $\beta V^{km}$  only through the three Flory-Huggins parameters, instead of all the six distinct  $\beta V^{km}$ .

The singular limit of  $\varepsilon^{-1} I_\varepsilon$  is  $J$ , initially defined on  $X_0$  or  $Y_0$  by

$$J(u) = \frac{1}{2} \sum_{k \neq m} e^{km} S_{km}(u) + \frac{\gamma}{2} \int_0^1 L(-\Delta)^{-\frac{1}{2}}(u - \bar{u}) \cdot (-\Delta)^{-\frac{1}{2}}(u - \bar{u}) dx. \quad (3.16)$$

The number of  $AB$  ( $BC$  and  $CA$  respectively) interfaces that  $u$  has is denoted by  $S_{AB}(u)$  ( $S_{BC}(u)$  and  $S_{CA}(u)$  respectively). The factor  $\frac{1}{2}$  in (3.16) takes care of double counting. We then extend the definition of  $J$  trivially to  $\hat{X}$  ( $\hat{Y}$  respectively) by setting  $J(u) = \infty$  if  $u \in \hat{X} \setminus X_0$  ( $\hat{Y} \setminus Y_0$  respectively).

At this point we prove that  $L$  is effectively positive definite so that  $\varepsilon^{-1} I_\varepsilon$  and  $J$  are both bounded from below by 0. Because of the constraint (2.6) which carries over to  $(-\Delta)^{-1/2}(u - \bar{u})$ , we restrict  $L$  to the 2-dimensional linear subspace

$$E = \{(z_A, z_B, z_C)^T \in \mathbf{R}^3 : z_A + z_B + z_C = 0\}.$$

**Lemma 3.4** *For every  $z \in E$  not equal to  $(0, 0, 0)^T$ ,  $Lz \cdot z > 0$ .*

*Proof.* If  $b_1$  and  $b_2$  form a basis in  $E$ ,  $L$  is represented by

$$L_E = \begin{bmatrix} b_1^T L b_1 & b_1^T L b_2 \\ b_2^T L b_1 & b_2^T L b_2 \end{bmatrix}.$$

To determine its positivity we temporarily choose  $b_1 = (1, -1, 0)^T$  and  $b_2 = (1, 0, -1)^T$ . Under this basis we find from (2.3) that

$$L_E = \frac{3}{2(ab + bc + ca)} \begin{bmatrix} \frac{b+c}{a^2} + \frac{c+a}{b^2} + \frac{2c}{ab} & \frac{b+c}{a^2} + \frac{c}{ab} + \frac{b}{ca} - \frac{a}{bc} \\ \frac{b+c}{a^2} + \frac{c}{ab} + \frac{b}{ca} - \frac{a}{bc} & \frac{b+c}{a^2} + \frac{b+c}{c^2} + \frac{2b}{ca} \end{bmatrix}.$$

It is positive definite since its determinant is  $\frac{9(a+b+c)^2}{4(ab+bc+ca)a^2b^2c^2} > 0$ .  $\square$

The theory of  $\Gamma$ -convergence, developed by De Giorgi [17], explains how  $\varepsilon^{-1}I_\varepsilon$  converges to  $J$  as  $\varepsilon \rightarrow 0$ . A large literature, including [31, 30, 26, 16, 1, 46, 48], exists for its application to local, Cahn-Hilliard [4] type problems, e.g. (2.1) with  $\sigma = 0$ . Applications to nonlocal problems are found in [42, 43], Ren and Truskinovsky [40], and Chmaj and Ren [8].

**Definition 3.5** Let  $F_\varepsilon$  and  $F_0$  be functionals defined on  $\hat{Z}$ .  $F_\varepsilon$  is said to  $\Gamma$ -converge to  $F_0$  if the following two statements hold.

1. For every family  $\{u_\varepsilon\} \subset \hat{Z}$  with  $\lim_{\varepsilon \rightarrow 0} u_\varepsilon = u$ ,  $\liminf_{\varepsilon \rightarrow 0} F_\varepsilon(u_\varepsilon) \geq F_0(u)$ ;
2. For every  $u \in \hat{Z}$ , there exists  $\{u_\varepsilon\} \subset \hat{Z}$  such that  $\lim_{\varepsilon \rightarrow 0} u_\varepsilon = u$  and  $\limsup_{\varepsilon \rightarrow 0} F_\varepsilon(u_\varepsilon) \leq F_0(u)$ .

**Proposition 3.6**  $\varepsilon^{-1}I_\varepsilon$   $\Gamma$ -converges to  $J$  in  $\hat{X}$  and  $\hat{Y}$ .

*Proof.* We isolate the local parts of  $I_\varepsilon$  and  $J$  to set, in the case of  $\hat{X}$ ,

$$\begin{aligned} I_{loc,\varepsilon}(u) &= \int_0^1 \left[ \frac{\varepsilon^2}{2} K u' \cdot u' + W(u) \right] dx \text{ if } u \in X, \infty \text{ if } u \in \hat{X} \setminus X, \\ J_{loc}(u) &= \frac{1}{2} \sum_{k \neq m} e^{km} S_{km}(u) \text{ if } u \in X_0, \infty \text{ if } u \in \hat{X} \setminus X_0. \end{aligned}$$

The case of  $\hat{Y}$  is treated in the same way.

It was proved in Baldo [1], Theorem 2.5, that  $\varepsilon^{-1}I_{loc,\varepsilon}$   $\Gamma$ -converges to  $J_{loc}$ . A few minor modifications are needed as we appeal to this result. First we have the matrix  $K$  in  $I_{loc,\varepsilon}$  instead of the identity matrix in [1]. This  $K$  leads to different  $e^{km}$  from the ones in [1]. Second we have the constraint (2.6) and the spaces  $\hat{X}$  and  $\hat{Y}$  reflect this restriction. Third the topology we use is induced by the  $L^2$ -norm instead of the  $L^1$ -norm in [1] and most other works on  $\Gamma$ -convergence.

Baldo's paper dealt with the more general domain  $D \subset \mathbf{R}^n$  where interfaces are co-dimension 1 surfaces. We refer to Sternberg [46, 47], [1], Fonseca and Tartar [16], and Sternberg and Zeimer [48] for more on higher dimensional, vector valued local problems. Here interfaces are just points in  $(0, 1)$  or  $\mathbf{R}/\mathbf{Z}$ .

Once we have the  $\Gamma$ -convergence of  $\varepsilon^{-1}I_{loc,\varepsilon}$  to  $J_{loc}$ , we add a continuous (in the sense of  $L^2$  norm) perturbation

$$u \in \hat{X} \rightarrow \frac{\gamma}{2} \int_0^1 L(-\Delta)^{-\frac{1}{2}}(u - \bar{u}) \cdot (-\Delta)^{-\frac{1}{2}}(u - \bar{u}) dx$$

to conclude from Definition 3.5 that  $\varepsilon^{-1}I_\varepsilon$   $\Gamma$ -converges to  $J$ .  $\square$

**Remark 3.7** If we drop the incompressibility condition (2.6) as mentioned in Remark 2.1,  $\varepsilon^{-1}I_\varepsilon$   $\Gamma$ -converges to the same  $J$ .

The next proposition is a uniform coercivity property.

**Proposition 3.8** Let  $\varepsilon_j$  be a sequence of positive numbers converging to 0, and  $\{u_j\}$  a sequence in  $\hat{X}$  ( $\hat{Y}$  respectively). If  $\varepsilon_j^{-1}I_{\varepsilon_j}(u_j)$  is bounded above in  $j$ , then  $\{u_j\}$  is relatively compact in  $\hat{X}$  ( $\hat{Y}$  respectively) and its cluster points belong to  $X_0$  ( $Y_0$  respectively).

*Proof.* See [42], Proposition 2.2.  $\square$

Following Propositions 3.6 and 3.8 is a persistent result, proved in Kohn and Sternberg [26]. It asserts that near an isolated local minimizer of the  $\Gamma$  limit  $F_0$  there exists a local minimizer of the perturbed  $F_\varepsilon$  if  $\varepsilon$  is small enough. We state two versions here. Denote an open ball in  $\hat{X}$  by

$$B_\delta(u_0) := \{u \in \hat{X} : \|u - u_0\| < \delta\}.$$

**Proposition 3.9** *Let  $\delta > 0$  and  $u_0 \in \hat{X}$  be such that  $J(u_0) < J(u)$  for all  $u \in B_\delta(u_0) \setminus \{u_0\}$ . Then there exist  $\varepsilon_0 > 0$  and  $u_\varepsilon \in B_{\delta/2}(u_0)$  for all  $\varepsilon < \varepsilon_0$  such that  $I_\varepsilon(u_\varepsilon) \leq I_\varepsilon(u)$  for all  $u \in B_{\delta/2}(u_0)$ . In addition  $\lim_{\varepsilon \rightarrow 0} \|u_\varepsilon - u_0\| = 0$ .*

*Proof.* See [26], Theorem 2.1.  $\square$

In  $\hat{Y}$  we must take care of the translation invariance of  $I_\varepsilon$ . Define a manifold of translates of  $u_0$

$$M(u_0) := \{u \in \hat{Y} : u(\cdot) = u_0(\cdot - y), y \in \mathbf{R}/\mathbf{Z}\}$$

and a tube like neighborhood of  $M(u_0)$

$$N_\delta(u_0) := \{u \in \hat{Y} : \|u(\cdot) - u_0(\cdot - y)\| < \delta, \text{ for some } y \text{ in } \mathbf{R}/\mathbf{Z}\}.$$

**Proposition 3.10** *Let  $\delta > 0$  and  $u_0 \in \hat{Y}$  be such that  $J(u_0) < J(u)$  for all  $u \in N_\delta(u_0) \setminus M(u_0)$ . Then there exist  $\varepsilon_0 > 0$  and  $u_\varepsilon \in N_{\delta/2}(u_0)$  for all  $\varepsilon < \varepsilon_0$  such that  $I_\varepsilon(u_\varepsilon) \leq I_\varepsilon(u)$  for all  $u \in N_{\delta/2}(u_0)$ . In addition  $u_\varepsilon \rightarrow u_0$  up to translation.*

*Proof.* Similar to the proof of the last proposition with some minor modification for the translation invariance.  $\square$

## 4 Periodic interval

We study  $I_\varepsilon$  in  $\hat{Y}$  in this section.

**Definition 4.1** *A pattern  $p$  of  $n$  layers is a closed loop of  $n$  letters of  $\{A, B, C\}$  modulo translation.  $p = \{p(i) \in \{A, B, C\} : i \in \mathbf{Z}_n, p(i) \neq p(i-1) \forall i\}$ . If  $p$  and  $q$  are two patterns of  $n$  layers and  $p(\cdot) = q(\cdot + j)$  for some  $j \in \mathbf{Z}_n$ ,  $p$  and  $q$  are considered to be the same pattern.*

**Definition 4.2** *For a pattern  $p$ ,  $Y_p$  is a set of  $u \in Y_0$  that agree with  $p$ . That is there exist  $y_0 = y_n, y_1, y_2, \dots, y_{n-1} \in \mathbf{R}/\mathbf{Z}$  and  $u(x) = (1, 0, 0)^T$  ( $(0, 1, 0)^T$  or  $(0, 0, 1)^T$  respectively) if  $x \in (y_{i-1}, y_i)$  and  $p(i) = A$  ( $B$  or  $C$  respectively),  $i = 1, 2, \dots, n$ .*

Every  $u \in Y_p$  is identified by its interfaces  $y_0, y_1, y_2, \dots, y_{n-1}$ . The space  $Y_0$  defined in Definition 3.2 is decomposed into mutually disjoint  $Y_p$ :

$$Y_0 = \cup_p Y_p. \tag{4.17}$$

The lamellar phase of the triblock copolymer has a specific pattern of structure. It is either  $p = ABCABC\dots$  or  $p = ACBACB\dots$  where  $A, B$  and  $C$  appear cyclically. Within each  $Y_p$  the  $\Gamma$ -limit  $J$  becomes a function of  $(y_0, y_1, \dots, y_{n-1})$ . The next proposition reduces the study of  $J$  from  $\hat{Y}$  to  $Y_p$ .

**Proposition 4.3** *If  $(y_0, y_1, \dots, y_{n-1})$  strictly minimizes  $J$  in  $Y_p$  locally, up to translation, then the corresponding  $u \in Y_p$  is a strict local minimizer of  $J$  in  $\hat{Y}$ , modulo translation.*

*Proof.* Suppose that the conclusion is false. There would be a sequence of  $u_j$  such that  $u_j \neq u \pmod{\mathbf{R}/\mathbf{Z}}$ ,  $u_j \rightarrow u$  and  $J(u_j) \leq J(u)$ . Since  $e^{km} S_{km}(u_j)$  remains bounded, i.e. the number of all interfaces of  $u_j$  is bounded from above by a constant,  $u_j$  must stay in a fixed, finite union of some  $Y_q$ . We may then assume without the loss of generality that all  $u_j \in Y_q$  for a pattern  $q$ .

According to the lower semicontinuity theorem of BV functions ([14], Theorem 1, p. 172),

$$\liminf_{j \rightarrow \infty} \frac{1}{2} \sum_{k \neq m} e^{km} S_{km}(u_j) \geq \frac{1}{2} \sum_{k \neq m} e^{km} S_{km}(u).$$

Combining this with  $J(u_j) \leq J(u)$  and the continuity of the nonlocal part of  $J$ , which implies

$$\lim_{j \rightarrow \infty} \frac{\gamma}{2} \int_0^1 L(-\Delta)^{-\frac{1}{2}}(u_j - \bar{u}_j) \cdot (-\Delta)^{-\frac{1}{2}}(u_j - \bar{u}_j) dx = \frac{\gamma}{2} \int_0^1 L(-\Delta)^{-\frac{1}{2}}(u - \bar{u}) \cdot (-\Delta)^{-\frac{1}{2}}(u - \bar{u}) dx,$$

we deduce that

$$\lim_{j \rightarrow \infty} \frac{1}{2} \sum_{k \neq m} e^{km} S_{km}(u_j) = \frac{1}{2} \sum_{k \neq m} e^{km} S_{km}(u). \quad (4.18)$$

Let us first consider the possibility  $q \neq p$ . Then  $u_j \rightarrow u$  implies that the  $p$  pattern may be obtained from the  $q$  pattern by ‘‘collapsing’’ a number of interfaces to each other. Therefore  $Y_q$  has more interfaces than  $Y_p$  does so that

$$\frac{1}{2} \sum_{k \neq m} e^{km} S_{km}(u_j) \geq \frac{1}{2} \sum_{k \neq m} e^{km} S_{km}(u) + \min\{e^{AB}, e^{BC}, e^{CA}\}.$$

The last inequality contradicts (4.18). The other possibility  $q = p$  is inconsistent with  $u_j \rightarrow u$  and the assumption of the proposition.  $\square$

In order to study  $J$  in  $Y_p$  we let

$$G(x) = \frac{x^2}{2} - \frac{x}{2} + \frac{1}{12}, \quad x \in (0, 1) \quad (4.19)$$

and periodically extended to  $\mathbf{R}$ , be the Green function of  $-G'' = \sum_{h \in \mathbf{Z}} \delta(\cdot - h) - 1$ , so that

$$v_k(x) := (-\Delta)^{-1}(u_k - \bar{u}_k)(x) = \int_0^1 G(x - y)(u_k(y) - \bar{u}_k) dy$$

is the 1-periodic solution of  $-v_k'' = u_k - \bar{u}_k$  on  $\mathbf{R}$  and  $\bar{v}_k = 0$ . With this  $v$  the nonlocal part of  $I_\varepsilon$  may be written alternatively as

$$\int_0^1 (-\Delta)^{-\frac{1}{2}}(u_k - \bar{u}_k)(-\Delta)^{-\frac{1}{2}}(u_m - \bar{u}_m) = \int_0^1 v_k' v_m' = \int_0^1 (u_k - \bar{u}_k)v_m.$$

Suppose that  $u \in Y_p$  is identified by the interfaces  $y_0, y_1, \dots, y_{n-1} \in \mathbf{R}/\mathbf{Z}$ . Here  $\mathbf{R}/\mathbf{Z}$  is regarded as a circle. We focus on the nonlocal part of  $J$  and define

$$H_{km}(y_0, \dots, y_{n-1}) = \int_0^1 (u_k - \bar{u}_k) v_m, \quad H(y_0, \dots, y_{n-1}) = \sum_{k,m} L^{km} H_{km}(y_0, \dots, y_{n-1}). \quad (4.20)$$

Note that  $J = \frac{1}{2} \sum_{k \neq m} e^{km} S_{km} + \frac{\gamma}{2} H$ . Denote the jump size of  $u_k$  at  $y_i$  by  $[u_k]_{y_i}$ , i.e.  $[u_k]_{y_i} := u_k(y_i+) - u_k(y_i-)$ .

**Lemma 4.4** 1. *The first derivative of  $H_{km}$  is*

$$\frac{\partial H_{km}}{\partial y_i} = -[u_k]_{y_i} v_m(y_i) - [u_m]_{y_i} v_k(y_i).$$

2. *The second derivative of  $H_{km}$  is*

$$\frac{\partial^2 H_{km}}{\partial y_j \partial y_i} = \begin{cases} -\sum_{h \neq i} ([u_k]_{y_i} [u_m]_{y_h} + [u_m]_{y_i} [u_k]_{y_h}) G(y_i - y_h), & i = j \\ ([u_k]_{y_i} [u_m]_{y_j} + [u_m]_{y_i} [u_k]_{y_j}) G(y_i - y_j), & i \neq j \end{cases}.$$

*Proof.* Differentiate  $H_{km}$  with respect to  $y_i$ .

$$\begin{aligned} \frac{\partial H_{km}}{\partial y_i} &= \frac{\partial}{\partial y_i} [\dots + \int_{y_{i-1}}^{y_i} (u_k - \bar{u}_k) v_m + \int_{y_i}^{y_{i+1}} (u_k - \bar{u}_k) v_m + \dots] \\ &= -[u_k]_{y_i} v_m(y_i) + \int_0^1 (u_k(x) - \bar{u}_k) \frac{\partial v_m(x)}{\partial y_i} dx. \end{aligned}$$

Moreover

$$\begin{aligned} \frac{\partial v_m(x)}{\partial y_i} &= \frac{\partial}{\partial y_i} \int_0^1 G(x - \cdot) (u_m - \bar{u}_m) \\ &= \frac{\partial}{\partial y_i} [\dots \int_{y_{i-1}}^{y_i} G(x - \cdot) (u_m - \bar{u}_m) + \int_{y_i}^{y_{i+1}} G(x - \cdot) (u_m - \bar{u}_m) \dots] \\ &= -[u_m]_{y_i} G(x - y_i). \end{aligned}$$

This yields part 1 of the lemma.

For the second derivative we first treat the off-diagonal elements. When  $j \neq i$ ,

$$\frac{\partial^2 H_{km}}{\partial y_j \partial y_i} = -[u_k]_{y_i} \frac{\partial v_m(y_i)}{\partial y_j} - [u_m]_{y_i} \frac{\partial v_k(y_i)}{\partial y_j}.$$

This leads us to calculate

$$\begin{aligned} \frac{\partial v_m(y_i)}{\partial y_j} &= \frac{\partial}{\partial y_j} [\dots \int_{y_{j-1}}^{y_j} G(y_i - \cdot) (u_m - \bar{u}_m) + \int_{y_j}^{y_{j+1}} G(y_i - \cdot) (u_m - \bar{u}_m) \dots] \\ &= -[u_m]_{y_j} G(y_i - y_j) \end{aligned}$$

and a similar expression for  $\frac{\partial v_k(y_i)}{\partial y_j}$ , which yield the mixed derivatives in part 2 of the lemma. When  $j = i$ ,

$$\frac{\partial^2 H_{km}}{\partial y_i^2} = -[u_k]_{y_i} \frac{\partial v_m(y_i)}{\partial y_i} - [u_m]_{y_i} \frac{\partial v_k(y_i)}{\partial y_i}.$$

So we compute

$$\begin{aligned} \frac{\partial v_m(y_i)}{\partial y_i} &= \frac{\partial}{\partial y_i} \left[ \dots \int_{y_{i-1}}^{y_i} G(y_i - \cdot) (u_m - \bar{u}_m) + \int_{y_i}^{y_{i+1}} G(y_i - \cdot) (u_m - \bar{u}_m) \dots \right] \\ &= -[u_m]_{y_i} G(0) + \int_0^1 G'(y_i - \cdot) (u_m - \bar{u}_m) \\ &= -[u_m]_{y_i} G(0) + \int_0^1 G(y_i - \cdot) u'_m = -[u_m]_{y_i} G(0) + \sum_{h=1}^n [u_m]_{y_h} G(y_i - y_h) \\ &= \sum_{h \neq i} [u_m]_{y_h} G(y_i - y_h) \end{aligned}$$

and a similar expression for  $\frac{\partial v_k(y_i)}{\partial y_i}$ . They lead to the pure derivatives in part 2. A matrix similar to this was observed in [8].  $\square$

Now let us consider the cyclic pattern  $p = ABCABC\dots ABC$  with  $n = 3\nu$  microdomains. So  $y_0$  is a  $CA$  interface,  $y_1$  an  $AB$  interface,  $y_2$  a  $BC$  interface, etc. Then Lemma 4.4 (1) and  $\frac{\partial H}{\partial y_i} = \sum_{k,m} L^{km} \frac{\partial H_{km}}{\partial y_i}$  yield

**Lemma 4.5** *The first derivative of  $H$  is*

$$\begin{aligned} \frac{\partial H}{\partial y_0} &= \frac{3[ca(c^2 - a^2)v_B(y_0) + ab(a^2 + ab + bc)v_C(y_0) - bc(c^2 + ab + bc)v_A(y_0)]}{(ab + bc + ca)a^2b^2c^2} \\ \frac{\partial H}{\partial y_1} &= \frac{3[ab(a^2 - b^2)v_C(y_1) + bc(b^2 + bc + ca)v_A(y_1) - ca(a^2 + bc + ca)v_B(y_1)]}{(ab + bc + ca)a^2b^2c^2} \\ \frac{\partial H}{\partial y_2} &= \frac{3[bc(b^2 - c^2)v_A(y_2) + ca(c^2 + ca + ab)v_B(y_2) - ab(b^2 + ca + ab)v_C(y_2)]}{(ab + bc + ca)a^2b^2c^2} \end{aligned}$$

and repeat over  $y_3, \dots, y_{3\nu-1}$ .

The second derivative of  $H$  follows from Lemma 4.4 (2) and that  $H'' = \sum_{k,m} L^{km} H''_{km}$ .

**Lemma 4.6** *The second derivative of  $H$  is*

$$\frac{\partial^2 H}{\partial y_i \partial y_j} = d_{ij} G(y_i - y_j) \text{ if } i \neq j, \text{ and } \frac{\partial^2 H}{\partial y_i^2} = - \sum_{j \neq i} d_{ij} G(y_i - y_j).$$

Here  $d_{ij}$  are constants determined in two cases depending on whether the interfaces at  $y_i$  and  $y_j$  are of the same type. If they are of different types, say  $y_i$  is a  $AB$  interface and  $y_j$  a  $BC$  interface,

$$d_{ij} = \frac{3}{(ab + bc + ca)abc} \left[ b^2 - c^2 - a^2 - \frac{ca(c + a)}{b} \right].$$

And if they are of the same type, say  $AB$ ,

$$d_{ij} = \frac{3}{(ab + bc + ca)abc} \left[ 2c^2 + \frac{bc(b+c)}{a} + \frac{ca(c+a)}{b} \right].$$

Other situations are described by similar formulae. Because of the cyclic nature of this pattern,  $d_{ij}$  only depends on the remainders of  $i$  and  $j$  divided by 3, i.e. if  $i \equiv s \pmod{3}$  and  $j \equiv t \pmod{3}$ , then  $d_{ij} = d_{st}$ . We place these distinct  $d_{st}$ ,  $s, t \in \{0, 1, 2\}$ , in a 3 by 3 matrix

$$\mathbf{d} := [d_{st}] = \frac{3}{(ab + bc + ca)abc} \cdot \begin{bmatrix} 2b^2 + \frac{ab(a+b)}{c} + \frac{bc(b+c)}{a} & a^2 - b^2 - c^2 - \frac{bc(b+c)}{a} & c^2 - a^2 - b^2 - \frac{ab(a+b)}{c} \\ a^2 - b^2 - c^2 - \frac{bc(b+c)}{a} & 2c^2 + \frac{bc(b+c)}{a} + \frac{ca(c+a)}{b} & b^2 - c^2 - a^2 - \frac{ca(c+a)}{b} \\ c^2 - a^2 - b^2 - \frac{ab(a+b)}{c} & b^2 - c^2 - a^2 - \frac{ca(c+a)}{b} & 2a^2 + \frac{ca(c+a)}{b} + \frac{ab(a+b)}{c} \end{bmatrix}. \quad (4.21)$$

Note that for any  $s \in \{0, 1, 2\}$ ,  $\sum_{t=0}^2 d_{st} = 0$ .

The constraints (2.5) give rise to three Lagrange multipliers  $\lambda_A$ ,  $\lambda_B$ , and  $\lambda_C$ , so at a critical point of  $H$

$$H'(y_0, y_1, \dots, y_{3\nu-1}) = (\lambda_C - \lambda_A, \lambda_A - \lambda_B, \lambda_B - \lambda_C, \lambda_C - \lambda_A, \lambda_A - \lambda_B, \dots)^T. \quad (4.22)$$

The equation (4.22) is satisfied by any translate of

$$(y_0, y_1, \dots, y_{3\nu-1}) = \left( 0, \frac{a}{\nu}, \frac{a+b}{\nu}, \frac{1}{\nu}, \frac{1+a}{\nu}, \frac{1+a+b}{\nu}, \frac{2}{\nu}, \dots, \frac{\nu-1+a+b}{\nu} \right), \quad (4.23)$$

by the symmetry in  $a, b, c$  of Lemma 4.5 and (4.22). This solution has the fine periodicity  $1/\nu$ . The word *fine* distinguishes this periodicity from the 1-periodicity in  $\hat{Y}$ .

The translation invariance of  $H$  is associated with the fact that 0 is an eigenvalue of  $H''$  and  $(1, 1, \dots, 1)^T$  is a corresponding eigenvector. If we let  $z = (z_0 = z_{3\nu}, z_1, \dots, z_{3\nu-1})^T$  be a perturbation of  $(y_0, y_1, \dots, y_{3\nu-1})^T$ , by (2.5) it must satisfy the constraints

$$\sum_{\zeta=0}^{\nu-1} (z_{3\zeta+1} - z_{3\zeta}) = \sum_{\zeta=0}^{\nu-1} (z_{3\zeta+2} - z_{3\zeta+1}) = \sum_{\zeta=0}^{\nu-1} (z_{3\zeta+3} - z_{3\zeta+2}) = 0. \quad (4.24)$$

Note that only two of the three equations in (4.24) are independent.

The key step in this paper is the following proposition. We postpone its difficult proof to the next section, where we will obtain more detailed spectral information of  $H''$  at (4.23).

**Proposition 4.7** *At (4.23) or any of its translates*

$$z^T H''(y_0, \dots, y_{3\nu-1}) z \geq 0$$

for all  $z$  satisfying (4.24) and the equality holds if and only if  $z \propto (1, 1, \dots, 1)^T$ . So (4.23) is a strict local minimum of  $H$  in  $Y_p$ , modulo translation.

We now state our main theorem.

**Theorem 4.8** For each  $\nu$ ,  $I_\varepsilon$  has a  $3\nu$  interface local minimizer  $u_{\nu,\varepsilon}$  of the cyclic  $p = ABC\dots ABC$  pattern when  $\varepsilon$  is small enough. More precisely as  $\varepsilon \rightarrow 0$ ,  $u_{\nu,\varepsilon} \rightarrow u_\nu$  in  $L^2$  norm where  $u_\nu \in Y_p$  is a translate of (4.23). Among these local minimizers  $I_\varepsilon$  favors the ones whose  $\nu$  are closest to

$$\nu_* := \left[ \frac{\gamma(5ab + 5bc + 5ca - 9abc)}{8(ab + bc + ca)(e^{AB} + e^{BC} + e^{CA})} \right]^{1/3}.$$

*Proof.* The existence of the local minimizers follows immediately from Propositions 3.10, 4.3 and 4.7. To determine which ones are more energetically favored, we need to find their energies. Start with the derivatives of  $v$  corresponding to the fine periodic solution (4.23).

$$\begin{aligned} v'_A(x) &= \begin{cases} (a-1)x + \frac{-a^2+a}{2\nu}, & x \in (0, \frac{a}{\nu}) \\ ax + \frac{-a^2-a}{2\nu}, & x \in (\frac{a}{\nu}, \frac{1}{\nu}) \end{cases}, \\ v'_B(x) &= \begin{cases} bx + \frac{-ab+bc}{2\nu}, & x \in (0, \frac{a}{\nu}) \\ (b-1)x + \frac{-ab+bc+2a}{2\nu}, & x \in (\frac{a}{\nu}, \frac{a+b}{\nu}) \\ bx + \frac{-ab+bc-2b}{2\nu}, & x \in (\frac{a+b}{\nu}, \frac{1}{\nu}) \end{cases}, \\ v'_C(x) &= \begin{cases} cx + \frac{c^2-c}{2\nu}, & x \in (0, \frac{a+b}{\nu}) \\ (c-1)x + \frac{(1-c)(2-c)}{2\nu}, & x \in (\frac{a+b}{\nu}, \frac{1}{\nu}) \end{cases}, \end{aligned}$$

and extended  $1/\nu$ -periodically to  $\mathbf{R}$ . With these expressions and the fact  $H_{km} = \int_0^1 v'_k v'_m$ , we find, after some lengthy calculation,

$$H(\nu) = \sum_{k,m} L^{km} H_{km}(\nu) = \frac{5ab + 5bc + 5ca - 9abc}{8(ab + bc + ca)\nu^2}.$$

Here we regard  $H$  as a function of  $\nu$ . Consequently

$$J(\nu) = (e^{AB} + e^{BC} + e^{CA})\nu + \frac{\gamma(5ab + 5bc + 5ca - 9abc)}{16(ab + bc + ca)\nu^2}. \quad (4.25)$$

If  $\nu$  is allowed to be any positive number in (4.25), then  $J(\nu)$  is convex in  $\nu$  and is minimized at  $\nu_*$  defined in the theorem. Denote the integer part of  $\nu_*$  by  $[\nu_*]$ . The solution (4.23) with  $\nu = [\nu_*]$  and the solution (4.23) with  $\nu = [\nu_*] + 1$  have lower  $J$  values than the solutions of other  $\nu$  do, and thus are more favored. Between these two, either one of them has lower  $J$ , or both of them have the same  $J$ , depending on the constants in (4.25).

$\nu_*$  is greater than 1 unless  $\gamma$  is very small. If  $\nu_* \leq 1$ , the three interface  $ABC$  pattern solution of (4.23) with  $\nu = 1$  is favored.  $\square$

**Remark 4.9** *Theorem 4.8 holds for the other cyclic pattern  $ACB\dots ACB$  as well. When we identify  $\mathbf{R}/\mathbf{Z}$  with a circle, we may think  $ABC\dots ABC$  as a clockwise pattern and  $ACB\dots ACB$  as a reversed counter-clockwise pattern. The reversal of (4.23) has the same energy.*

To interpret Theorem 4.8 we note that if we choose  $\gamma$  not too small, the most favored  $\nu$  is  $\approx \nu_*$  and  $1/\nu_*$  is the combined thickness of an  $ABC$  cycle of three microdomains in the scaled domain  $D = (0, 1)^3$ . As we return to the real domain  $\Omega = (0, d)^3$ , by (2.8) the thickness of an  $ABC$  cycle is

$$\frac{d}{\nu_*} = lN^{2/3} \left[ \frac{4(ab + bc + ca)(e^{AB} + e^{BC} + e^{CA})}{3\sqrt{6}(5ab + 5bc + 5ca - 9abc)} \right]^{1/3}. \quad (4.26)$$

The surface tension terms  $e^{km}$  may be taken to be (3.14) if the unmodified  $W$  of (2.4) is preferred.

The study of cyclic patterns with the number of interfaces not divisible by 3 is more difficult. An even harder question is to determine the global minimizer(s) of  $J$  or  $I_\varepsilon$ . One has to consider all possible patterns in  $\hat{Y}$ , not just the cyclic ones. Our speculation is in the following conjecture.

**Conjecture 4.10** *Any global minimizer of  $J$  has a cyclic pattern.*

## 5 Spectral analysis

We turn to the hard work of analyzing the spectrum of the second derivative matrix of  $H$  at (4.23). We establish the following result from which Proposition 4.7 follows immediately.

**Proposition 5.1**  *$H''$  at (4.23) has eigenvalue 0 corresponding to an eigenvector  $(1, 1, 1, \dots, 1, 1, 1)$ . It may also have two negative eigenvalues. But eigenvectors corresponding to these two eigenvalues are perpendicular to the subspace defined by (4.24). The remaining  $3\nu - 3$  eigenvalues are all positive.*

*Proof.* It is more convenient to study the spectrum of  $H''$  in the complex space  $\mathbf{C}^n$ . In this context  $i$  is the imaginary unit. Taking the expression from Lemma 4.6 we decompose

$$H'' = \mathbf{E} + \mathbf{F}.$$

The  $(j, k)$  entry of  $\mathbf{E}$  is  $d_{jk}G(y_j - y_k)$  where  $d_{jk}$  is defined in (4.21), and  $(y_0, \dots, y_{3\nu-1})$  are given in (4.23). The matrix  $\mathbf{F}$  is diagonal. Its  $(j, j)$  entry is  $-\sum_{k=0}^{n-1} d_{jk}G(y_j - y_k)$ . Recall that  $d_{jk}$  only depends on  $(s, t)$  where  $s, t$  are the remainders of  $j, k$  divided by 3. Let us divide  $\mathbf{E}$  and  $\mathbf{F}$  into 3 by 3 blocks:

$$\mathbf{E} = \begin{bmatrix} \mathbf{e}_{00} & \mathbf{e}_{01} & \dots & \mathbf{e}_{0(\nu-1)} \\ \mathbf{e}_{10} & \mathbf{e}_{11} & \dots & \mathbf{e}_{1(\nu-1)} \\ \dots & \dots & \dots & \dots \\ \mathbf{e}_{(\nu-1)0} & \mathbf{e}_{(\nu-1)1} & \dots & \mathbf{e}_{(\nu-1)(\nu-1)} \end{bmatrix}, \quad \mathbf{F} = \begin{bmatrix} \mathbf{f} & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & \mathbf{f} & \dots & \mathbf{0} \\ \dots & \dots & \dots & \dots \\ \mathbf{0} & \mathbf{0} & \dots & \mathbf{f} \end{bmatrix}$$

where  $\mathbf{0}$  is the 3 by 3 zero matrix. In  $\mathbf{E}$  these blocks are labeled by indices  $\beta, \xi \in \{0, 1, \dots, \nu - 1\}$ . A typical  $\mathbf{e}_{\beta\xi}$  is

$$\mathbf{e}_{\beta\xi} := \begin{bmatrix} d_{00}g_{3\beta,3\xi} & d_{01}g_{3\beta,1+3\xi} & d_{02}g_{3\beta,2+3\xi} \\ d_{10}g_{1+3\beta,3\xi} & d_{11}g_{1+3\beta,1+3\xi} & d_{12}g_{1+3\beta,2+3\xi} \\ d_{20}g_{2+3\beta,3\xi} & d_{21}g_{2+3\beta,1+3\xi} & d_{22}g_{2+3\beta,2+3\xi} \end{bmatrix}.$$

Here we write  $g_{s+3\beta, t+3\xi}$  for  $G(y_{s+3\beta} - y_{t+3\xi})$  at (4.23).  $\mathbf{f}$  is a diagonal 3 by 3 matrix. By (4.19) and (4.21) we deduce

$$\mathbf{f} = \begin{bmatrix} \frac{d_{02}(c-c^2)+d_{01}(a-a^2)}{2\nu} & 0 & 0 \\ 0 & \frac{d_{10}(a-a^2)+d_{12}(b-b^2)}{2\nu} & 0 \\ 0 & 0 & \frac{d_{20}(c-c^2)+d_{21}(b-b^2)}{2\nu} \end{bmatrix}.$$

The spectral analysis is done in two steps. First we perform a ‘‘coarse’’ discrete Fourier transform to convert  $H''$  to a matrix with vanishing off-diagonal 3 by 3 blocks. In the second step we study the spectra of the diagonal blocks.

The coarse discrete Fourier transform is given by the matrix  $\mathbf{P}$  whose  $(\alpha, \beta)$  block is

$$\frac{1}{\sqrt{\nu}} \exp(-2\pi i \frac{\alpha\beta}{\nu}) \mathbf{I}_3, \quad \alpha, \beta \in \{0, 1, \dots, \nu - 1\}, \quad (5.27)$$

where  $\mathbf{I}_3$  is the 3 by 3 identity matrix.  $\mathbf{P}$  is unitary so its inverse  $\mathbf{P}^{-1}$  is its adjoint, i.e. (5.27) with the  $-2\pi i$ 's replaced by  $2\pi i$ 's in the exponents.

It is easy to see that  $\mathbf{P}\mathbf{F}\mathbf{P}^{-1} = \mathbf{F}$ . The calculation of  $\mathbf{P}\mathbf{E}\mathbf{P}^{-1}$  is more involved. The  $(\alpha, \eta)$  block of this product is

$$\sum_{\beta, \xi} \frac{1}{\nu} \exp(-2\pi i \frac{\alpha\beta}{\nu} + 2\pi i \frac{\xi\eta}{\nu}) \mathbf{e}_{\beta\xi}. \quad (5.28)$$

The computation of (5.28) is done on the entries of  $\mathbf{e}_{\beta\xi}$  individually, so for any  $s, t \in \{0, 1, 2\}$  the  $(s, t)$  entry of (5.28) is

$$\frac{d_{st}}{\nu} \sum_{\beta, \xi} \exp(-2\pi i \frac{\alpha\beta}{\nu} + 2\pi i \frac{\xi\eta}{\nu}) g_{s+3\beta, t+3\xi}. \quad (5.29)$$

We start with

$$\sum_{\beta} \exp(-2\pi i \frac{\alpha\beta}{\nu}) g_{s+3\beta, t+3\xi}, \quad (5.30)$$

which up to a factor is the  $(s, t)$  entry of the  $(\alpha, \xi)$  block of  $\mathbf{P}\mathbf{E}$ . When  $\alpha = 0$ , we use (4.19) to find that (5.30) is

$$\sum_{\beta} g_{s+3\beta, t+3\xi} = \sum_{\zeta=0}^{\nu-1} G(y_s - y_t + \frac{\zeta}{\nu}) = \begin{cases} \frac{6a^2-6a+1}{12\nu} & \text{if } |y_s - y_t| = \frac{a}{\nu} \\ \frac{6b^2-6b+1}{12\nu} & \text{if } |y_s - y_t| = \frac{b}{\nu} \\ \frac{6c^2-6c+1}{12\nu} & \text{if } |y_s - y_t| = \frac{a+b}{\nu} \\ \frac{1}{12\nu} & \text{if } y_s = y_t \end{cases}, \quad (5.31)$$

a quantity independent of  $\xi$ . When  $\alpha \neq 0$ , we use an indirect method. Apply a discrete negative Laplace operator to  $g_{s+3\beta, t+3\xi}$  regarded as a function of  $\beta$ , so by (4.19)

$$\begin{aligned} & 2g_{s+3\beta, t+3\xi} - g_{s+3(\beta-1), t+3\xi} - g_{s+3(\beta+1), t+3\xi} \\ &= \begin{cases} -(1/\nu)^2 + |y_s - y_t| & \text{if } \beta - \xi \equiv 1 \pmod{\nu} \text{ and } y_s - y_t < 0 \\ -(1/\nu)^2 + |y_s - y_t| & \text{if } \beta - \xi \equiv -1 \pmod{\nu} \text{ and } y_s - y_t > 0 \\ -(1/\nu)^2 + (1/\nu) - |y_s - y_t| & \text{if } \beta = \xi \\ -(1/\nu)^2 & \text{otherwise} \end{cases}. \end{aligned}$$

After multiplying the two sides of the last equation by  $\exp(-2\pi i \frac{\alpha\beta}{\nu})$  and summing over  $\beta$ , we deduce

$$\begin{aligned} & (2 - 2 \cos(\frac{2\pi\alpha}{\nu})) \sum_{\beta} \exp(-2\pi i \frac{\alpha\beta}{\nu}) g_{s+3\beta, t+3\xi} \\ &= (\frac{1}{\nu} - |y_s - y_t|) \exp(-2\pi i \frac{\alpha\xi}{\nu}) + |y_s - y_t| \exp(-2\pi i \frac{\alpha(\xi \mp 1)}{\nu}) \end{aligned}$$

where  $-$  is used if  $y_s - y_t > 0$  and  $+$  is used otherwise. Therefore when  $\alpha \neq 0$ , (5.30) is

$$\frac{1}{2 - 2 \cos(\frac{2\pi\alpha}{\nu})} [(\frac{1}{\nu} - |y_s - y_t|) \exp(-2\pi i \frac{\alpha\xi}{\nu}) + |y_s - y_t| \exp(-2\pi i \frac{\alpha(\xi \mp 1)}{\nu})].$$

Finally we multiply (5.31) and the last quantity by  $\exp(2\pi i \frac{\xi\eta}{\nu})$  and sum over  $\xi$  to find (5.29):

$$\begin{aligned} & (s, t) \text{ entry of } (\alpha, \eta) \text{ block of } \mathbf{PEP}^{-1} \tag{5.32} \\ &= \begin{cases} d_{st} \sum_{\zeta=0}^{\nu-1} G(y_s - y_t + \frac{\zeta}{\nu}), & \alpha = \eta = 0 \\ \frac{d_{st}}{2 - 2 \cos(\frac{2\pi\alpha}{\nu})} [\frac{1}{\nu} - |y_s - y_t| + |y_s - y_t| \exp(\pm 2\pi i \frac{\alpha}{\nu})], & \alpha = \eta \geq 1 \\ 0, & \alpha \neq \eta \end{cases} \end{aligned}$$

In the exponent of the right side we take  $+$  if  $y_s - y_t > 0$  and  $-$  if  $y_s - y_t \leq 0$ .

This way  $H''$  is diagonalized to

$$\mathbf{M} = \begin{bmatrix} \mathbf{m}_0 & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & \mathbf{m}_1 & \dots & \mathbf{0} \\ \dots & & & \\ \mathbf{0} & \mathbf{0} & \dots & \mathbf{m}_{\nu-1} \end{bmatrix} := \mathbf{P}H''\mathbf{P}^{-1} = \mathbf{PEP}^{-1} + \mathbf{F}.$$

The  $\mathbf{m}_\alpha$  blocks in  $\mathbf{M}$  are obtained from (5.32) and  $\mathbf{f}$ .  $\mathbf{m}_0$  is

$$\frac{1}{12\nu} \begin{bmatrix} \dots & d_{01}(6a^2 - 6a + 1) & d_{02}(6c^2 - 6c + 1) \\ d_{10}(6a^2 - 6a + 1) & \dots & d_{12}(6b^2 - 6b + 1) \\ d_{20}(6c^2 - 6c + 1) & d_{21}(6b^2 - 6b + 1) & \dots \end{bmatrix}, \tag{5.33}$$

where the unspecified diagonal entries are  $(\mathbf{m}_0)_{ss} = -\sum_{t \neq s} (\mathbf{m}_0)_{st}$ . For  $\alpha \geq 1$ ,

$$\mathbf{m}_\alpha = \mathbf{f} + \frac{1}{(2 - 2 \cos(\frac{2\pi\alpha}{\nu}))\nu}. \tag{5.34}$$

$$\begin{bmatrix} d_{00} & d_{01}(1 - a + a \exp(-2\pi i \frac{\alpha}{\nu})) & d_{02}(1 - (a + b) + (a + b) \exp(-2\pi i \frac{\alpha}{\nu})) \\ \dots & d_{11} & d_{12}(1 - b + b \exp(-2\pi i \frac{\alpha}{\nu})) \\ \dots & \dots & d_{22} \end{bmatrix}.$$

The unspecified  $(1, 0)$ ,  $(2, 0)$  and  $(2, 1)$  entries are respectively the complex conjugates of the  $(0, 1)$ ,  $(0, 2)$  and  $(1, 2)$  entries by the self-adjointness of  $\mathbf{M}$ . This completes the first step of our spectral analysis of  $H''$ .

In the second step we study the spectra of  $\mathbf{m}_\alpha$ . Obviously one of the eigenvalues of  $\mathbf{m}_0$  is 0, whose eigenvector is  $(1, 1, 1, \dots, 1, 1, 1)^T$ . The signs of the other two eigenvalues of  $\mathbf{m}_0$  depend on  $a$ ,  $b$  and  $c$ . Fortunately these two eigenvalues are irrelevant. Note that the invariant subspace corresponding to  $\mathbf{m}_0$  is the linear span of the first three columns of  $\mathbf{P}$  defined in (5.27), i.e.

$$c_1(1, 0, 0, \dots, 1, 0, 0)^T + c_2(0, 1, 0, \dots, 0, 1, 0)^T + c_3(0, 0, 1, \dots, 0, 0, 1)^T.$$

In this 3-dimensional linear space we find the 2-dimensional subspace vertical to  $(1, 1, 1, \dots, 1, 1, 1)^T$ :

$$c_4(-1, 1, 0, \dots, -1, 1, 0)^T + c_5(0, -1, 1, \dots, 0, -1, 1)^T.$$

This subspace is also generated by the eigenvectors of the other two eigenvalues, and is the orthogonal complement of the subspace defined by the constraints (4.24).

**Remark 5.2** *Our numerical calculation shows that the two eigenvalues are negative when  $a$ ,  $b$  and  $c$  are all close to  $1/3$ , and may be positive otherwise.*

More difficult to prove is that the eigenvalues of  $\mathbf{m}_\alpha$ ,  $\alpha \geq 1$ , are all positive. We do so by showing that  $\mathbf{m}_\alpha$  is positive definite. Let

$$\tilde{a} = b^2 + c^2 - a^2 + \frac{bc(b+c)}{a}, \quad \tilde{b} = c^2 + a^2 - b^2 + \frac{ca(c+a)}{b}, \quad \tilde{c} = a^2 + b^2 - c^2 + \frac{ab(a+b)}{c}.$$

So  $(\tilde{a}, \tilde{b}, \tilde{c}) \propto (-d_{01}, -d_{12}, -d_{02})$ . Up to a positive factor  $\mathbf{m}_\alpha$  is

$$\begin{aligned} & \begin{bmatrix} \tilde{c}(1 - (1 - \cos \theta)(c - c^2)) + \tilde{a}(1 - (1 - \cos \theta)(a - a^2)) \\ -\tilde{a}(1 - a + ae^{i\theta}) \\ -\tilde{c}(1 - a - b + (a + b)e^{i\theta}) \end{bmatrix} ; \\ & \begin{bmatrix} -\tilde{a}(1 - a + ae^{-i\theta}) \\ \tilde{a}(1 - (1 - \cos \theta)(a - a^2)) + \tilde{b}(1 - (1 - \cos \theta)(1 - (b - b^2))) \\ -\tilde{b}(1 - b + be^{i\theta}) \end{bmatrix} ; \\ & \begin{bmatrix} -\tilde{c}(1 - a - b + (a + b)e^{-i\theta}) \\ -\tilde{b}(1 - b + be^{-i\theta}) \\ \tilde{b}(1 - (1 - \cos \theta)(1 - (b - b^2))) + \tilde{c}(1 - (1 - \cos \theta)(c - c^2)) \end{bmatrix} \end{aligned} \quad (5.35)$$

where  $\theta = 2\pi\alpha/\nu \in (0, 2\pi)$ .

We separate two cases of (5.35). In the first case all  $\tilde{a}, \tilde{b}, \tilde{c} \geq 0$ . We prove that the diagonal elements dominate the off-diagonal elements. Take the first row for instance. With  $t = 1 - \cos \theta \in (0, 2]$ , and  $1 - (a - a^2)t$ , etc,  $> 0$ ,

$$\begin{aligned} & |(\mathbf{m}_\alpha)_{00}| - |(\mathbf{m}_\alpha)_{01}| - |(\mathbf{m}_\alpha)_{02}| \\ & \propto \tilde{c}(1 - (1 - \cos \theta)(c - c^2)) + \tilde{a}(1 - (1 - \cos \theta)(a - a^2)) \\ & \quad - \tilde{a}|1 - a + ae^{i\theta}| - \tilde{c}|1 - a - b + (a + b)e^{-i\theta}| \\ & = \tilde{c}[1 - (c - c^2)t - \sqrt{1 - 2(c - c^2)t}] + \tilde{a}[1 - (a - a^2)t - \sqrt{1 - 2(a - a^2)t}]. \end{aligned}$$

The two quantities in the brackets are positive, and at least one of  $\tilde{a}$  and  $\tilde{c}$  is positive since  $\tilde{a} + \tilde{c} > 0$ . Therefore the last line is positive and  $\mathbf{m}_\alpha$  is positive definite.

In the second case one of  $\tilde{a}, \tilde{b}, \tilde{c}$  is negative. We show that the nested minors of the matrix (5.35) are all positive. The (0,0) entry of the matrix is

$$\begin{aligned} & (b^2 + c^2 - a^2 + \frac{bc(b+c)}{a})(1 - (a - a^2)t) + (a^2 + b^2 - c^2 + \frac{ab(a+b)}{c})(1 - (c - c^2)t) \\ &= (b^2 + \frac{bc(b+c)}{a})(1 - (a - a^2)t) + (b^2 + \frac{ab(a+b)}{c})(1 - (c - c^2)t) \\ &\quad + (a^2 - c^2)(a - c - a^2 + c^2)t \\ &> \frac{a^2b}{c}(1 - (c - c^2)t) > 0. \end{aligned}$$

The term in the second last line is non-negative since it may be factored to  $(a-c)^2(a+c)(1-a-c)t \geq 0$ . The lower bound  $\frac{a^2b}{c}(1 - (c - c^2)t)$  is not necessary for this estimate, but useful for the next one. Similarly the (1,1) entry may be bounded from below by  $\frac{a^2c}{b}(1 - (b - b^2)t)$ .

Next we show that the 2 by 2 minor corresponding to the (1,1) entry is positive. First assume that  $\tilde{a} < 0$ . This means that  $a$  is sufficiently large. In particular  $a > b$  and  $a > c$ . Using the lower bounds on the (0,0) and (1,1) entries, we deduce

$$\begin{aligned} & (\mathbf{m}_\alpha)_{00}(\mathbf{m}_\alpha)_{11} - (\mathbf{m}_\alpha)_{01}^2 \\ & \propto [\tilde{a}(1 - (c - c^2)t) + \tilde{c}(1 - (c - c^2)t)] \cdot [\tilde{a}(1 - (c - c^2)t) + \tilde{b}(1 - (b - b^2)t)] - \tilde{a}^2(1 - 2a(1 - a)t) \\ & > a^4(1 - (c - c^2)t)(1 - (b - b^2)t) - a^4(1 - 2a(1 - a)t) \\ & = a^4(a - c - a^2 + c^2 + a - b - a^2 + b^2)t = a^4((a - c)b + (a - b)c)t \geq 0. \end{aligned}$$

The other two possibilities  $\tilde{b} < 0$  and  $\tilde{c} < 0$  may be handled by arguing in the same way with the minors corresponding to the (1,1) and (2,2) entries.

Finally we show that the determinant of (5.35) is positive. A careful calculation shows that the determinant is  $t^2$  multiplied by

$$\begin{aligned} & [\tilde{c}(1 - (c - c^2)t) + \tilde{a}(1 - (a - a^2)t)]\tilde{b}^2(b - b^2)^2 \\ & + [\tilde{a}(1 - (a - a^2)t) + \tilde{b}(1 - (b - b^2)t)]\tilde{c}^2(c - c^2)^2 \\ & + [\tilde{b}(1 - (b - b^2)t) + \tilde{c}(1 - (c - c^2)t)]\tilde{a}^2(a - a^2)^2 \\ & + 2\tilde{a}\tilde{b}\tilde{c}[(a - a^2)(b - b^2) + (b - b^2)(c - c^2) + (c - c^2)(a - a^2) - 2abc - abc(1 - a)(1 - b)(1 - c)t]. \end{aligned}$$

The last quantity is linear in  $t$ . Its derivative with respect to  $t$  is

$$-[\tilde{c}(c - c^2) + \tilde{a}(a - a^2)] \cdot [\tilde{a}(a - a^2) + \tilde{b}(b - b^2)] \cdot [\tilde{b}(b - b^2) + \tilde{c}(c - c^2)].$$

Note that

$$\begin{aligned} & \tilde{a}(a - a^2) + \tilde{c}(c - c^2) \\ &= a(b^2 + c^2)(b + c) - a^3(b + c) + bc(b + c)^2 + c(b^2 + a^2)(a + b) - c^3(a + b) + ab(a + b)^2 \\ &= 2ab^2c + abc^2 + a^2bc + b^3c + bc^3 + a^3b + ab^3 + 2a^2b^2 + 2b^2c^2 > 0. \end{aligned} \tag{5.36}$$

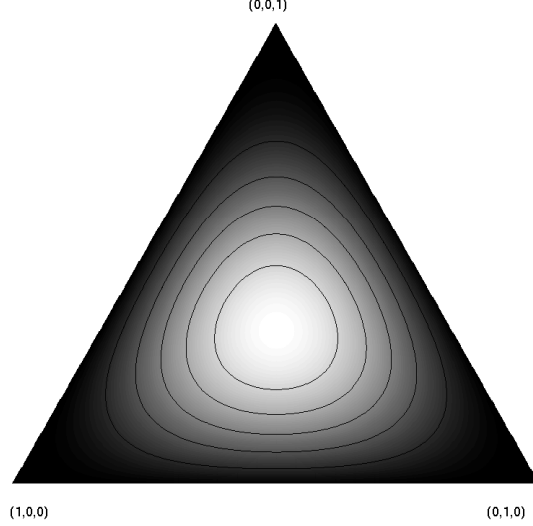


Figure 1: The domain and some level curves of the determinant of (5.37) as a function of  $(a, b, c)$ .

Similarly

$$\tilde{a}(a - a^2) + \tilde{b}(b - b^2) > 0, \quad \tilde{b}(b - b^2) + \tilde{c}(c - c^2) > 0.$$

This implies that  $t^{-2}$  times the determinant of (5.35) is decreasing in  $t$ . So it suffices to show that the determinant is positive when  $t = 2$ , i.e.  $\theta = \pi$ . At this  $\theta$  the matrix (5.35) becomes

$$\begin{bmatrix} \hat{c} + \hat{a} & -\hat{a}z_1 & -\hat{c}z_3 \\ -\hat{a}z_1 & \hat{a} + \hat{b} & -\hat{b}z_2 \\ -\hat{c}z_3 & -\hat{b}z_2 & \hat{b} + \hat{c} \end{bmatrix}, \quad (5.37)$$

where

$$\hat{a} = \tilde{a}(1 - 2(a - a^2)), \quad \hat{b} = \tilde{b}(1 - 2(b - b^2)), \quad \hat{c} = \tilde{c}(1 - 2(c - c^2)),$$

and

$$z_1 = \frac{1 - 2a}{1 - 2(a - a^2)}, \quad z_2 = \frac{1 - 2b}{1 - 2(b - b^2)}, \quad z_3 = \frac{1 - 2(a + b)}{1 - 2(c - c^2)}.$$

In Figure 1 the determinant of (5.37) is viewed as a function of  $(a, b, c)$ .  $(a, b, c)$  is restricted on the depicted triangle  $a + b + c = 1$ ,  $a, b, c > 0$ . Some numerically calculated level curves are drawn. Note that the determinant is zero on the boundary of the triangle, positive inside, and attains the maximum value at  $a = b = c = 1/3$ . The rigorous proof of the positivity is rather tedious, so we leave it in the appendix.  $\square$

## 6 Bounded interval

We study  $I_\varepsilon$  in  $\hat{X}$  in this section.

**Definition 6.1** A pattern is a finite sequence  $p = \{p(1), p(2), \dots, p(n)\}$  with  $p(i) \in \{A, B, C\} \forall i = 1, 2, \dots, n$ , and  $p(i) \neq p(i-1) \forall i = 2, 3, \dots, n$ .

**Definition 6.2** For a pattern  $p$ ,  $X_p$  is a set of  $u \in X_0$  for which there exist  $x_1, x_2, \dots, x_{n-1} \in (0, 1)$  and  $u(x) = (1, 0, 0)^T$  ( $(0, 1, 0)^T$  or  $(0, 0, 1)^T$  respectively) if  $x \in (x_{i-1}, x_i)$  and  $p(i) = A$  ( $B$  or  $C$  respectively),  $i = 1, 2, 3, \dots, n$ . Here  $x_0 = 0$  and  $x_n = 1$ .

Every  $u \in X_p$  is identified by its interfaces  $x_1, x_2, \dots, x_{n-1}$ . The space  $X_0$  defined in Definition 3.1 is decomposed into mutually disjoint sets:  $X_0 = \cup_p X_p$ .

**Proposition 6.3** If  $(x_1, x_2, \dots, x_{n-1})$  strictly minimizes  $J$  in  $X_p$  locally, then the corresponding  $u \in X_p$  is a strict local minimizer of  $J$  in  $\hat{X}$ .

*Proof.* The only difference from the proof of Proposition 3.10 is that interfaces of a member in  $X_q$ , analogous to  $Y_q$ , may “collapse” to the boundary points 0 and 1 as well as to each other.  $\square$

Combined with Proposition 3.9, this proposition allows us to show the existence of local minimizers of  $I_\varepsilon$  for small  $\varepsilon$  near strict local minimizers of  $J$  in  $X_p$ . It turns out that unlike (4.23) in  $\hat{Y}$ ,  $J$  does not have perfectly fine periodic solutions in  $\hat{X}$ . This is also in contrast to the diblock copolymer problem where local minimizers in the analogy of  $\hat{X}$  are all finely periodic [42]. We illustrate this point by finding some sample local minimizers.

As in Section 4 we again define the nonlocal part of  $J$  in  $X_p$  by  $H$ .

$$H(x_1, \dots, x_{n-1}) := \sum_{k,m} L^{km} \int_0^1 v'_k v'_m, \quad (6.38)$$

so  $J = \frac{1}{2} \sum_{k \neq m} e^{km} S_{km} + \frac{\gamma}{2} H$ . Here  $v_k(x) = (-\Delta)^{-1}(u_k - \bar{u}_k)$ . We proceed to find a more explicit expression for  $H$ . Let  $x_0 = 0$  and  $x_n = 1$ . Set  $r_j = x_j - x_{j-1}$ ,  $\forall j = 1, 2, \dots, n$ . In each  $(x_{j-1}, x_j)$  denote the constant value of  $u_k - \bar{u}_k$  by  $U_{k,j}$ . We also define the vectors  $U_j = (U_{A,j}, U_{B,j}, U_{C,j})^T$ . Each  $U_j$  assumes one of the three values  $(1-a, -b, -c)^T$ ,  $(-a, 1-b, -c)^T$ , and  $(-a, -b, 1-c)^T$ . Also  $U_j \neq U_{j+1}$ ,  $\forall j = 1, 2, \dots, n-1$ . We write down  $v'_k$  explicitly. For  $x \in (x_{j-1}, x_j)$

$$-v'_k(x) = U_{k,j}(x - x_{j-1}) + \sum_{i=1}^{j-1} U_{k,i} r_i,$$

so that

$$\begin{aligned} \int_{x_{j-1}}^{x_j} v'_k v'_m dx &= \int_{x_{j-1}}^{x_j} [U_{k,j}(x - x_{j-1}) + \sum_{h=1}^{j-1} U_{k,h} r_h] \cdot [U_{m,j}(x - x_{j-1}) + \sum_{i=1}^{j-1} U_{m,i} r_i] dx \\ &= U_{k,j} U_{m,j} \frac{r_j^3}{3} + \sum_{h=1}^{j-1} U_{k,h} U_{m,j} r_h \frac{r_j^2}{2} + \sum_{i=1}^{j-1} U_{k,j} U_{m,i} r_i \frac{r_j^2}{2} + \sum_{h=1}^{j-1} \sum_{i=1}^{j-1} U_{k,h} U_{m,i} r_h r_i r_j \\ &= U_{k,j} U_{m,j} \frac{r_j^3}{3} + \frac{1}{2} \sum_{h=1}^{j-1} \sum_{i=1}^j U_{k,h} U_{m,i} r_h r_i r_j + \frac{1}{2} \sum_{h=1}^j \sum_{i=1}^{j-1} U_{k,h} U_{m,i} r_h r_i r_j. \end{aligned}$$

We sum over  $j, k$  and  $m$  to find  $H$  as a function of  $(r_1, \dots, r_n)$ :

$$H(r_1, \dots, r_n) = \sum_{j=1}^n \frac{q_{jj}}{3} r_j^3 + \sum_{j=1}^n \sum_{h=1}^{j-1} \sum_{i=1}^j q_{hi} r_h r_i r_j \quad (6.39)$$

where we have defined  $q_{hi} = \sum_{k,m} L^{km} U_{k,h} U_{m,i}$ , which are placed in an  $n$  by  $n$  matrix  $\mathbf{Q} = [q_{hi}]$ .

**Lemma 6.4** *If for  $h, i \in \{1, \dots, n\}$   $U_{s,h} = 1 - \bar{u}_s$  and  $U_{t,i} = 1 - \bar{u}_t$ , then  $q_{hi} = L^{st}$ .*

*Proof.*

$$q_{hi} = \sum_{k,m} L^{km} U_{k,h} U_{m,i} = L^{st} + \sum_k L^{kt} (-\bar{u}_k) + \sum_m L^{sm} (-\bar{u}_m) + \sum_{k,m} L^{km} (-\bar{u}_k) (-\bar{u}_m) = L^{st}.$$

The last equation follows because the three sums are all zero, a consequence of a property of  $L$  in (2.3):  $L(a, b, c)^T = (0, 0, 0)^T$ .  $\square$

Throughout the rest of the section we assume for simplicity that

$$a = b = c = 1/3. \quad (6.40)$$

In this case  $H$  is further simplified by the next lemma.

**Lemma 6.5** *Define  $\tilde{q}_{hi} = 1$  if  $U_h = U_i$  and 0 otherwise. Place  $\tilde{q}_{hi}$  in an  $n$  by  $n$  matrix  $\tilde{\mathbf{Q}} = [\tilde{q}_{hi}]$ . Let*

$$H_1(r_1, \dots, r_n) = \sum_{j=1}^n r_j^3 + 3 \sum_{j=1}^n \sum_{h=1}^{j-1} \sum_{i=1}^j \tilde{q}_{hi} r_h r_i r_j.$$

*Then under (6.40)  $H(\cdot) \propto \tilde{H}(\cdot) - 1/3$ .*

*Proof.* When (6.40) holds,

$$L \propto \begin{bmatrix} 2 & -1 & -1 \\ -1 & 2 & -1 \\ -1 & -1 & 2 \end{bmatrix}.$$

This turns (6.39) to

$$\begin{aligned} H(r_1, \dots, r_n) &\propto \frac{2}{3} \sum_{j=1}^n r_j^3 - \sum_{j=1}^n \sum_{h=1}^{j-1} \sum_{i=1}^j r_h r_i r_j + 3 \sum_{j=1}^n \sum_{h=1}^{j-1} \sum_{i=1}^j \tilde{q}_{hi} r_h r_i r_j \\ &= \frac{2}{3} \sum_{j=1}^n r_j^3 - \frac{1}{3} \left[ \left( \sum_{j=1}^n r_j \right)^3 - \sum_{j=1}^n r_j^3 \right] + 3 \sum_{j=1}^n \sum_{h=1}^{j-1} \sum_{i=1}^j \tilde{q}_{hi} r_h r_i r_j = \tilde{H}(r_1, \dots, r_n) - \frac{1}{3}. \end{aligned}$$

Here we have used the identity

$$\sum_{j=1}^n \sum_{h=1}^{j-1} \sum_{i=1}^j r_h r_i r_j = \frac{1}{3} \left[ \left( \sum_{j=1}^n r_j \right)^3 - \sum_{j=1}^n r_j^3 \right],$$

which follows from a simple induction argument.  $\square$

The constraints (2.5) require that  $n \geq 3$ . When  $n = 3$  the trivial local minimizers of  $\tilde{H}$  are the lone elements

$$r_1 = r_2 = r_3 = \frac{1}{3} \text{ in } X_{ABC}, \quad (6.41)$$

and in the  $X_p$  where  $p$  is one of the five permutations of  $ABC$ .

Nontrivial cases appear when  $n = 4$ . One typical pattern is  $ABCA$ . In this case

$$\tilde{\mathbf{Q}} = \begin{bmatrix} 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 1 \end{bmatrix}.$$

By Lemma 6.5 and (2.5) which implies  $r_2 = r_3 = 1/3$  and  $r_4 = (1/3) - r_1$ , we deduce

$$\begin{aligned} \tilde{H}(\cdot) &= r_1^3 + r_2^3 + r_3^3 + r_4^3 + 3r_2r_1^2 + 3r_3(r_1^2 + r_2^2) + 3r_4(r_1^2 + r_2^2 + r_3^2 + r_1r_4) \\ &= r_1^3 + \frac{2}{27} + \left(\frac{1}{3} - r_1\right)^3 + r_1^2 + \left(r_1^2 + \frac{1}{9}\right) + 3\left(\frac{1}{3} - r_1\right)\left(\frac{2}{9} + \frac{r_1}{3}\right). \end{aligned}$$

From the last expression we obtain  $d\tilde{H}/dr_1 = 4r_1 - 2/3$ . This yields a single local minimum of  $\tilde{H}$  at  $r_1 = 1/6$ , i.e.

$$r_1 = \frac{1}{6}, \quad r_2 = r_3 = \frac{1}{3}, \quad r_4 = \frac{1}{6} \text{ in } X_{ABCA}; \quad \tilde{H}(r_1 = \frac{1}{6}) = \frac{7}{18}. \quad (6.42)$$

The second typical pattern is a non-cyclic  $ABCB$ . Here

$$\tilde{\mathbf{Q}} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \end{bmatrix}.$$

A similar calculation shows that a local minimum exists at

$$r_1 = \frac{1}{3}, \quad r_2 = \frac{1}{6}, \quad r_3 = \frac{1}{3}, \quad r_4 = \frac{1}{6} \text{ in } X_{ABCB}; \quad \tilde{H}(r_2 = \frac{1}{6}) = \frac{5}{12}. \quad (6.43)$$

Note that this local minimum has higher  $\tilde{H}$  value.

When  $n = 5$  we first study a cyclic pattern  $ABCAB$ . For this case

$$\tilde{\mathbf{Q}} = \begin{bmatrix} 1 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 1 \end{bmatrix}.$$

The constraints (2.5) force  $r_3 = 1/3$ ,  $r_4 = (1/3) - r_1$ , and  $r_5 = (1/3) - r_2$ . We view

$$\begin{aligned} \tilde{H}(\cdot) &= \sum_{i=1}^5 r_i^3 + 3r_2r_1^2 + 3r_3(r_1^2 + r_2^2) \\ &\quad + 3r_4(r_1^2 + r_2^2 + r_3^2 + r_1r_4) + 3r_5(r_1^2 + r_2^2 + r_3^2 + r_4^2 + 2r_1r_4 + r_2r_5) \end{aligned}$$

as a function of  $r_1$  and  $r_2$ . The derivative of  $\tilde{H}$  is

$$\tilde{H}' = \begin{pmatrix} 6r_1r_2 - 3r_2^2 + 2r_1 - 1/3 \\ 3r_1^2 - 6r_1r_2 + 4r_2 - 2/3 \end{pmatrix}.$$

We find a local minimum numerically at

$$r_1 = .14088, r_2 = .19245, r_3 = .33333, r_4 = .19245, r_5 = .14088 \text{ in } X_{ABCAB}; \quad \tilde{H}(\dots) = .35891. \quad (6.44)$$

The second pattern we consider is a non-cyclic  $ABCBA$ , for which

$$\tilde{\mathbf{Q}} = \begin{bmatrix} 1 & 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

The constraints (2.5) force  $r_3 = 1/3$ ,  $r_5 = (1/3) - r_1$ , and  $r_4 = (1/3) - r_2$ . We view

$$\begin{aligned} \tilde{H}(\cdot) &= \sum_{i=1}^5 r_i^3 + 3r_2r_1^2 + 3r_3(r_1^2 + r_2^2) + 3r_4(r_1^2 + r_2^2 + r_3^2 + r_2r_4) \\ &\quad + 3r_5(r_1^2 + r_2^2 + r_3^2 + r_4^2 + 2r_2r_4 + r_1r_5) \end{aligned}$$

as a function of  $r_1$  and  $r_2$ . The derivatives with respect to  $r_1$  and  $r_2$  are

$$\tilde{H}' = \begin{pmatrix} 4r_1 - 2/3 \\ 2r_2 - 1/3 \end{pmatrix}, \quad H'' = \begin{bmatrix} 4 & 0 \\ 0 & 2 \end{bmatrix}.$$

Hence there exists a unique local minimum at

$$r_1 = r_2 = \frac{1}{6}, r_3 = \frac{1}{3}, r_4 = r_5 = \frac{1}{6} \text{ in } X_{ABCBA}; \quad \tilde{H}(\dots) = \frac{13}{36}. \quad (6.45)$$

This one has higher  $\tilde{H}$  value than the last one.

When  $n = 6$ , we consider  $ABCABC$ . Now

$$\tilde{\mathbf{Q}} = \begin{bmatrix} 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 \\ 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 \end{bmatrix}.$$

Our numerical calculation finds a local minimum at

$$\begin{aligned} r_1 = .10210, r_2 = .16667, r_3 = .23124, r_4 = .23124, r_5 = .16667, \\ r_6 = .10210 \text{ in } X_{ABCABC}; \quad \tilde{H}(\dots) = .34954. \end{aligned} \quad (6.46)$$

Next we take a non-cyclic pattern  $ABCACB$ , so

$$\tilde{\mathbf{Q}} = \begin{bmatrix} 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

A local minimum is found at

$$\begin{aligned} r_1 = .10184, r_2 = .18754, r_3 = .21759, r_4 = .23150, r_5 = .11575, \\ r_6 = .14580 \text{ in } X_{ABCACB}; \tilde{H}(\dots) = .35197 \end{aligned} \quad (6.47)$$

which has higher  $\tilde{H}$  value than the last one.

A cyclic pattern with  $n = 7$  is  $ABCABCA$  whose

$$\tilde{\mathbf{Q}} = \begin{bmatrix} 1 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 1 \end{bmatrix}.$$

We find a local minimum at

$$\begin{aligned} r_1 = .08734, r_2 = .13013, r_3 = .20320, r_4 = .15866, r_5 = .20320, \\ r_6 = .13013, r_7 = .08734 \text{ in } X_{ABCABCA}; \tilde{H}(\dots) = .34406. \end{aligned} \quad (6.48)$$

Motivated by the fine “anti-symmetry” of (6.45) we take up another anti-symmetric pattern  $p = ABCACBA$ , for which

$$\tilde{\mathbf{Q}} = \begin{bmatrix} 1 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 1 & 0 & 0 & 1 \end{bmatrix}.$$

Interestingly there is a local minimum with fine anti-symmetry at

$$2r_1 = r_2 = r_3 = r_4 = r_5 = r_6 = 2r_7 = \frac{1}{6} \text{ in } X_{ABCACBA}; \tilde{H}(\dots) = \frac{25}{72}. \quad (6.49)$$

This one again has higher  $\tilde{H}$  value than the last cyclic one.

Observing (6.41 - 6.49), we pose the following conjecture.

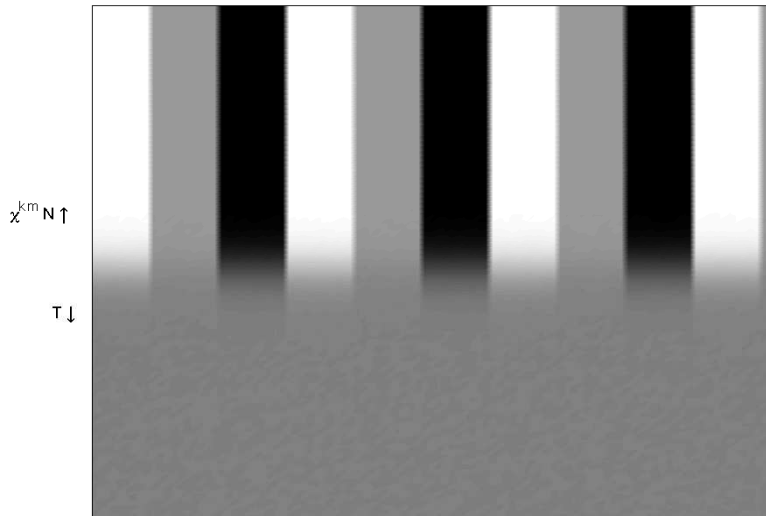


Figure 2: Disorder to ordered lamellar phase transition as  $\chi^{km}N \rightarrow \infty$ .

**Conjecture 6.6** *When  $\varepsilon$  is small, local minimizers with cyclic patterns have lower  $I_\varepsilon$  free energy than the non-cyclic ones with the same numbers of AB, BC and CA interfaces. The global minimizers of  $I_\varepsilon$  are cyclic.*

However these cyclic minimizers, (6.44), (6.46) and (6.48), do not have perfect fine symmetry like in (4.23). The local minimizers with fine anti-symmetry, i.e. (6.45) and (6.49), on the other hand, are not cyclic and have higher  $J$  values.

## 7 Discussion

It was shown in [45], Propositions 6.1 and 6.2, that the disordered phase described by the constant critical point  $(a, b, c)^T$  of  $I_\varepsilon$  is stable if and only if, in the notation of this paper,  $\sqrt{\varepsilon^2 \varepsilon \gamma} = 1/N$  is large compared to the Flory-Huggins parameters (3.15), i.e. if and only if  $\chi^{AB}N$ ,  $\chi^{BC}N$  and  $\chi^{CA}N$  are all small. In this paper when we hold  $\chi^{km}$  fixed and take  $\varepsilon \rightarrow 0$  which is equivalent to  $N \rightarrow \infty$ ,  $\chi^{km}N$  all become large. So as depicted in Figure 2 the disordered phase of high symmetry, characterized by the infinite group  $\mathbf{R}/\mathbf{Z} \simeq SO(2)$ , is no longer stable. It gives way to the lamellar phase, an ordered phase of lower symmetry represented by the finite subgroup  $\{g \in \mathbf{R}/\mathbf{Z} : 3\nu g = 0\} \simeq \mathbf{Z}_{3\nu}$ . Equivalently if we hold  $N$  fixed but temperature  $1/\beta$  variable, then by (3.15) since  $\chi^{km}$  are proportional to  $\beta$ , large  $\chi^{km}N$  correspond to low temperature, as the physics of second order phase transitions tells us. Therefore we have obtained a mathematical model of this theory in triblock copolymers.

This approach to phase transitions is more direct than the traditional one that deals with the thermodynamic limit in the entire space. Here we study on a bounded domain. Phase transitions are directly shown in the order parameter instead of being interpreted from the non-analyticity points in thermodynamic variables. Phase transitions occur over a fuzzy region rather than across a

sharp boundary. We believe that our method may be applied to other second order phase transition problems such as solidification of a fluid from a disordered homogeneous phase to a crystalline lattice structure.

The distinct feature in our model (2.1) or (2.9) is the nonlocal term. Without it the lamellar structure can not exist (Carr, Gurtin and Slemrod [6]), a fact well-known in Cahn-Hilliard type problems. A different nonlocal term was used in [40] to study an elastic bar with a stable oscillatory strain field.

The formula (4.26), which states that the thickness of lamellar microdomains is of order  $d \sim N^{2/3}l$ , is consistent with the result obtained for diblock copolymers in [42] under the same choice of  $d$ . In general the triblock copolymer problem is far more complex. In the diblock copolymer problem there is only one way to arrange lamellar microdomains: ...*ABABAB*..., while in the triblock copolymer problem the choices are infinite.

The concavity requirement of  $(\beta V^{km}/2)z_k z_m$  in Section 2 is not always met in triblock copolymers. According to [45] if we take the same basis for  $E$  as in the proof of Lemma 3.4, the second derivative of  $(\beta V^{km}/2)z_k z_m$  restricted on  $P$  is

$$\begin{bmatrix} -2\chi^{AB} & -\chi^{AB} - \chi^{CA} + \chi^{BC} \\ -\chi^{AB} - \chi^{CA} + \chi^{BC} & -2\chi^{CA} \end{bmatrix}.$$

Clearly one eigenvalue of this matrix is negative since the trace is negative. But the determinant is

$$2\chi^{AB}\chi^{BC} + 2\chi^{BC}\chi^{CA} + 2\chi^{CA}\chi^{AB} - (\chi^{AB})^2 - (\chi^{BC})^2 - (\chi^{CA})^2$$

which may not be positive. To have concavity, the three Flory-Huggins parameters must be reasonably comparable in their sizes. Otherwise we have a double well problem, i.e.  $W$  in (2.9) has two global minima on  $P$ . One well represents concentration of one monomer type but the other well represents a mixture of the other two monomer types. This becomes similar to the diblock copolymer problem.

Once 1-dimensional local minimizers are found, it is natural to extend them trivially to a 3-dimensional box and one hopes that they model the lamellar phase in reality. But this is not so simple. It was shown in the diblock copolymer case by the authors [44] that a 1-D local minimizer of the diblock copolymer problem is a 3-D local minimizer only if the the number of its interfaces is large enough, or the similar  $\gamma$  in the the diblock copolymer problem is small enough. Only 3-D local minimizers, termed meta-stable states in physics, can be morphology phases of block copolymers. The 1-D global minimizer, analogous to the one found in Theorem 4.8, lies near the borderline that separates the meta-stable lamellar solutions from the non-meta-stable lamellar solutions. We expect the same to be true in the triblock copolymer problem.

The free energy functional (2.1) may be written in a local form with second order derivatives. The work of Müller [33] deals with such a local functional which can be converted to the free energy functional of the diblock copolymer problem under the condition  $a = b = 1/2$ . We feel that the nonlocal formulation is more natural. Using the nonlocal setting in [41] we generalized the result of [33] to any  $a \in (0, 1)$ .

**Acknowledgments.** We thank Professors R. Kohn and C. Muratov for several stimulating conversations on the subject of block copolymers during the 50th annual SIAM conference in Philadelphia.

## References

- [1] S. Baldo. Minimal interface criterion for phase transitions in mixtures of Cahn-Hilliard fluids. *Ann. Inst. H. Poincaré Anal. Non Linéaire*, 7(2):67–90, 1990.
- [2] F.S. Bates and G.H. Fredrickson. Block copolymers - designer soft materials. *Physics Today*, 52(2):32–38, 1999.
- [3] V.Y. Borue and I.Y. Erukhimovich. A statistical theory of weakly charged polyelectrolytes: fluctuations, equation of state and microphase separation. *Macromolecules*, 21(11):3240–3249, 1988.
- [4] J.W. Cahn and J.E. Hilliard. Free energy of a nonuniform system. I. Interfacial free energy. *J. Chem. Phys.*, 28(2):258–267, 1958.
- [5] C.M. Care and N.H. March. Electron crystalization. *Adv. Phys.*, 24(1):101–116, 1975.
- [6] J. Carr, M.E. Gurtin, and M. Slemrod. Structured phase transitions on a finite interval. *Arch. Rational Mech. Anal.*, 86(4):317–351, 1984.
- [7] L.Q. Chen and A.G. Khachatryan. Dynamics of simultaneous ordering and phase separation and effect of long-range Coulomb interactions. *Phys. Rev. Lett.*, 70(10):1477–1480, 1993.
- [8] A. Chmaj and X. Ren. Multiple layered solutions of the nonlocal bistable equation. *Phys. D*, 147(1-2):135–154, 2000.
- [9] R. Choksi. Scaling laws in microphase separation of diblock copolymers. *J. Nonlinear Sci.*, 11:223–236, 2001.
- [10] P.G. de Gennes. *J. de Physique-Lett*, 40:69, 1979.
- [11] P.G. de Gennes. *Scaling Concepts in Polymer Physics*. Cornell University Press, Ithaca, NY, 1979.
- [12] V.J. Emery and S.A. Kivelson. Frustrated electronic phase separation and high-temperature superconductors. *Physica C*, 209:597–621, 1993.
- [13] I.Y. Erukhimovich and A.R. Khokhlov. Microphase separation in polymer systems: new approaches and objects. *Polymer Sci.*, 35(11):1522–1531, 1993.
- [14] L.C. Evans and R.F. Gariepy. *Measure Theory and Fine Properties of Functions*. CRC Press, Boca Raton, New York, London, Tokyo, 1992.
- [15] P.C. Fife and D. Hilhorst. The Nishiura-Ohnishi free boundary problem in the 1D case. *SIAM J. Math. Anal.*, 33(3):589–606, 2001.
- [16] I. Fonseca and L. Tartar. The gradient theory of phase transitions for systems with two potential wells. *Proc. Roy. Soc. Edinburgh Sect. A*, 111(1-2):89–102, 1989.
- [17] E. De Giorgi. Sulla convergenza di alcune successioni di integrali del tipo della'area. *Rendiconti di Matematica*, 8:277–294, 1975.

- [18] A.Y. Grosberg and A.R. Khokhlov. *Statistical Physics of Macromolecules*. American Institute of Physics, New York, 1994.
- [19] E. Helfand. Theory of inhomogeneous polymers: fundamentals of Gaussian random-walk model. *J. Chem. Phys.*, 62(3):999–1005, 1975.
- [20] E. Helfand and Z.R. Wasserman. Block copolymer theory. 4. narrow interphase approximation. *Macromolecules*, 9(6):879–888, 1976.
- [21] E. Helfand and Z.R. Wasserman. Block copolymer theory. 5. spherical domains. *Macromolecules*, 11(5):960–966, 1978.
- [22] E. Helfand and Z.R. Wasserman. Block copolymer theory. 6. cylindrical domains. *Macromolecules*, 13(4):994–998, 1980.
- [23] M. Henry. Singular limit of a fourth order problem arising in the micro-phase separation of diblock copolymers. *Adv. Differential Equations*, 6(9):1049–1114, 2001.
- [24] K.M. Hong and J. Noolandi. Theory of inhomogeneous multicomponent polymer systems. *Macromolecules*, 14(3):727–736, 1981.
- [25] K.M. Hong and J. Noolandi. Theory of phase equilibria in systems containing block copolymers. *Macromolecules*, 16(7):1083–1093, 1983.
- [26] R. Kohn and P. Sternberg. Local minimisers and singular perturbations. *Proc. Royal Soc. Edin.*, 111A:69–84, 1989.
- [27] L. Leibler. Theory of microphase separation in block copolymers. *Macromolecules*, 13(6):1602–1617, 1980.
- [28] R.F. Mamin. Domain structure of a new type near a photostimulated phase transition; autosolitons. *JETP Lett*, 60(1):52–56, 1994.
- [29] M.W. Matsen and M. Schick. Stable and unstable phases of a diblock copolymer melt. *Phys. Rev. Letters*, 31(16):2660–2663, 1994.
- [30] L. Modica. The gradient theory of phase transitions and the minimal interface criterion. *Arch. Rat. Mech. Anal.*, 98:357–383, 1987.
- [31] L. Modica and S. Mortola. Un esempio di  $\Gamma^-$ -convergenza. *Boll. Un. Mat. Ital. B (5)*, 14(1):285–299, 1977.
- [32] Y. Mogi, M. Nomura, H. Kotsuji, K. Ohnishi, Y. Matsushita, and I. Noda. Superlattice structures in morphologies of the ABC triblock copolymers. *Macromolecules*, 27(23):6755–6760, 1994.
- [33] S. Müller. Singular perturbations as a selection criterion for periodic minimizing sequences. *Calc. Var. Partial Differential Equations*, 1(2):169–204, 1993.
- [34] C.B. Muratov. Theory of domain patterns in systems with long-range interactions of Coulomb type. *Phys. Rev. E*, to appear.

- [35] H. Nakazawa and T. Ohta. Microphase separation of ABC-type triblock copolymers. *Macromolecules*, 26(20):5503–5511, 1993.
- [36] Y. Nishiura and I. Ohnishi. Some mathematical aspects of the microphase separation in diblock copolymers. *Phys. D*, 84:31–39, 1995.
- [37] I.A. Nyrkova, A.R. Khokhlov, and M. Doi. Microdomain structures in polyelectrolyte systems: calculation of the phase diagrams by direct minimization of the free energy. *Macromolecules*, 27(15):4220–4230, 1994.
- [38] I. Ohnishi, Y. Nishiura, M. Imai, and Y. Matsushita. Analytical solutions describing the phase separation driven by a free energy functional containing a long-range interaction term. *Chaos*, 9(2):329–341, 1999.
- [39] T. Ohta and K. Kawasaki. Equilibrium morphology of block copolymer melts. *Macromolecules*, 19(10):2621–2632, 1986.
- [40] X. Ren and L. Truskinovsky. Finite scale microstructures in nonlocal elasticity. In recognition of the sixtieth birthday of Roger L. Fosdick (Blacksburg, VA, 1999). *J. Elasticity*, 59(1-3):319–355, 2000.
- [41] X. Ren and J. Wei. On energy minimizers of the di-block copolymer problem. preprint.
- [42] X. Ren and J. Wei. On the multiplicity of solutions of two nonlocal variational problems. *SIAM J. Math. Anal.*, 31(4):909–924, 2000.
- [43] X. Ren and J. Wei. Concentrically layered energy equilibria of the di-block copolymer problem. *European J. Appl. Math.*, 13(5):479–496, 2002.
- [44] X. Ren and J. Wei. On the spectra of 3-D lamellar solutions of the diblock copolymer problem. *SIAM J. Math. Anal.*, to appear.
- [45] X. Ren and J. Wei. Triblock copolymer theory: Free energy, disordered phase and weak segregation. *Phys. D*, to appear.
- [46] P. Sternberg. The effect of a singular perturbation on nonconvex variational problems. *Arch. Rational Mech. Anal.*, 101(3):209–260, 1988.
- [47] P. Sternberg. Vector-valued local minimizers of nonconvex variational problems. Current directions in nonlinear partial differential equations (Provo, UT, 1987). *Rocky Mountain J. Math.*, 21(2):799–807, 1991.
- [48] P. Sternberg and W. Zeimer. Local minimisers of a three-phase partition problem with triple junctions. *Proc. Roy. Soc. Edinburgh Sect. A*, 124(6):1059–1073, 1994.
- [49] F.H. Stillinger. Variational model for micelle structure. *J. Chem. Phys.*, 78(7):4654–4661, 1983.

## Appendix

Since the determinant of the matrix (5.37) is symmetric in  $a, b, c$ , we assume without the loss of generality that  $\tilde{a} < 0$ . Elementary column operations turn (5.37) to

$$\begin{bmatrix} \hat{c} + \hat{a} & 0 & 0 \\ -\hat{a}z_1 & \hat{a} + \hat{b} - \frac{\hat{a}^2 z_1^2}{\hat{c} + \hat{a}} & -\hat{b}z_2 - \frac{\hat{c}\hat{a}z_3 z_1}{\hat{c} + \hat{a}} \\ -\hat{c}z_3 & -\hat{b}z_2 - \frac{\hat{c}\hat{a}z_3 z_1}{\hat{c} + \hat{a}} & \hat{b} + \hat{c} - \frac{\hat{c}^2 z_3^2}{\hat{b} + \hat{c}} \end{bmatrix}$$

without altering its determinant. Note that  $a > c$  implies  $1 - 2(a - a^2) < 1 - 2(c - c^2)$ . So  $\tilde{c} + \tilde{a} > 0$  yields  $\hat{c} + \hat{a} > 0$ . Now it suffices to show that

$$[(\hat{c} + \hat{a})(\hat{a} + \hat{b}) - \hat{a}z_1^2] \cdot [(\hat{c} + \hat{a})(\hat{b} + \hat{c}) - \hat{c}z_3^2] > [\hat{b}(\hat{c} + \hat{a})z_2 + \hat{a}\hat{c}z_1 z_3]^2. \quad (\text{A.1})$$

For the left hand side of (A.1),  $\hat{a} + \hat{b} > 0$  implies

$$\text{LHS of (A.1)} \geq [S - \hat{c}\hat{a}\sqrt{1 - z_1^2}\sqrt{1 - z_3^2}]^2$$

where

$$S = \hat{a}\hat{b} + \hat{b}\hat{c} + \hat{c}\hat{a} = (\hat{c} + \hat{a})(\hat{a} + \hat{b}) - \hat{a}^2 > 0$$

by the same reasoning as in estimating the 2 by 2 minor in Section 5. The right hand side of (A.1) can be written as

$$\text{RHS of (A.1)} = [S - 2b^2(\tilde{b}(\hat{c} + \hat{a}) + \tilde{c}\tilde{a}) - \hat{c}\hat{a}\sqrt{1 - z_1^2}\sqrt{1 - z_3^2}]^2.$$

So to obtain (A.1), we show that  $\tilde{b}(\hat{c} + \hat{a}) + \tilde{c}\tilde{a} > 0$ , which is equivalent to

$$(\tilde{a} + \tilde{c})(\tilde{a} + \tilde{b}) - \tilde{a}^2 > 2\tilde{b}(\tilde{a}a(1 - a) + \tilde{c}c(1 - c)). \quad (\text{A.2})$$

We prove this by contradiction. Suppose that (A.2) is false.

We first claim that  $a > 1/2 > b + c$ . Suppose  $a \leq 1/2$ . Since (A.2) does not hold, we must have

$$\tilde{b}(\tilde{a}((1 - a)^2 + a^2) + \tilde{c}((1 - c)^2 + c^2)) + \tilde{a}\tilde{c} \leq 0. \quad (\text{A.3})$$

But

$$\begin{aligned} \tilde{b}(\tilde{a}((1 - a)^2 + a^2) + \tilde{c}((1 - c)^2 + c^2)) &> \tilde{b}(\tilde{a} + \tilde{c})(a^2 + b^2 + c^2) \\ &> \frac{ac(a + c)}{b}(2b^2 + \frac{ab(a + b)}{c} + \frac{bc(b + c)}{a})(a^2 + b^2) \\ &> 2b^2 \frac{ac(a + c)}{b}(b^2 + a^2 + \frac{ab(a + b)}{c}) > 2abc\tilde{c}. \end{aligned}$$

Thus (A.3) implies that

$$a^2 > b^2 + c^2 + \frac{bc(b + c)}{a} + 2abc > b^2 + c^2 + (\frac{1 - a}{a} + 2a)bc > (b + c)^2.$$

This implies  $a > 1/2$ , a contradiction to the assumption  $a \leq 1/2$ . Therefore we obtain  $a > 1/2 > b + c$ .

Next we estimate the two sides of (A.2).

$$\begin{aligned}
& (\tilde{a} + \tilde{c})(\tilde{a} + \tilde{b}) - \tilde{a}^2 & (A.4) \\
& > \left(2b^2 + \frac{ab(a+b)}{c} + \frac{bc(b+c)}{a}\right) \left(2c^2 + \frac{ac(a+c)}{b} + \frac{bc(b+c)}{a}\right) - (a^2 - (b^2 + c^2))^2 \\
& > a^3(b+c) + a^2bc + 2a^2(b^2 + c^2) + 2abc(1+a) + 2b^2c^2 + ab^2c + (b^2 + c^2)(ab + bc + ca).
\end{aligned}$$

Since

$$\tilde{a}a(b+c) + \tilde{c}c(a+b) = 2ab^2 + bc(a+c+b^2-c^2) < 2ab^2 + bc,$$

we deduce that

$$\begin{aligned}
2\tilde{b}(\tilde{a}a(1-a) + \tilde{c}c(1-c)) &= 2\tilde{b}(\tilde{a}a(b+c) + \tilde{c}c(a+b)) < 2(a^2(b+c) + c^2(a+b))(2ab+c) \\
&< 2a^3b(b+c) + 2a^3b(b+c) + 2a^2c(b+c) + 4abc^2(a+b) + 2c^3(a+b).
\end{aligned}$$

Comparing the last inequality and (A.4), we have

$$\begin{aligned}
& [(\tilde{a} + \tilde{b})(\tilde{a} + \tilde{c}) - \tilde{a}^2] - [2\tilde{b}(\tilde{a}a(1-a) + \tilde{c}c(1-c))] \\
& > a^3(a-b+c)(b+c) + 2a^2b(b+c)^2 + 2abc + 2b^2c^2 + ab^2c - a^2bc - 4abc^2(a+b) - c^3(a+b) \\
& > 2a^3c(b+c) + 2a^2bc^2 + 2abc + 2b^2c^2 + ab^2c - a^2bc - 4abc^2(a+b) - c^3(a+b) \\
& > (2a^3bc - a^2bc) + (2a^3c^2 - c^3a) + (2a^2bc^2 - bc^3) + (2abc - 4a^2bc^2) + (2b^2c^2 + ab^2c - 4ab^2c^2) \\
& > a^2bc(2a-1) + ac^2(2a^2-c) + bc^2(2a^2-c) + 2abc(1-2ac) + ((2-2a)b^2c^2 + ab^2c(1-2c)) \\
& > 0.
\end{aligned}$$

Here in the second last line the first term is positive since  $2a > 1$ . The second and third terms are positive since  $2a^2 > 1/2 > c$ . The fourth and the last terms are positive since  $2c < 1$ . This contradicts the assumption that (A.2) is false.