

Concentrically Layered Energy Equilibria of the Di-Block Copolymer Problem

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December, 2001

Abstract

We prove the existence of energy equilibria of the di-block copolymer problem in the unit disk. They consist of concentrically layered micro-domains rich in one of the two monomer building units. We construct them by solving the proper singular limit of the free energy functional. The same limit also explains how under a dynamic law of the free energy, circular interfaces of non-equilibria may move to the origin and vanish, or collapse to each other, thereby reducing the number of layers.

1 Introduction

A di-block copolymer is a linear-chain molecule consisting of two sub-chains a and b grafted covalently to each other. The sub-chains a and b are made of different monomer units A and B , respectively. In polymer systems even a weak repulsion between unlike monomers A and B induces a strong repulsion between a and b . As a result the different sub-chains tend to segregate below some temperature T_c , but as they are chemically bonded, even a complete segregation of sub-chains a and b cannot lead to a macroscopic phase separation. Only a local micro-phase separation occurs: micro-domains rich in A and B are formed. See Bates and Fredrickson [2] for an introduction to block copolymers.

*Supported in part by NSF grant DMS-9703727.

†Supported in part by an Earmarked Grant of RGC, Hong Kong.

A thermal equilibrium model based on the free energy was given by Leibler in [11] and Ohta and Kawasaki in [17]. Later Bahiana and Oono [1] derived this energy through a cell dynamical system approach. It takes the form

$$F(u) = \int_{\Omega} \left[\frac{\epsilon^2}{2} |\nabla u|^2 + W(u) + \frac{\sigma}{2} |(-\Delta)^{-1/2}(u - m)|^2 \right] dx \quad (1.1)$$

in the admissible set

$$X_m = \left\{ u \in W^{1,2}(\Omega) : \frac{1}{|\Omega|} \int_{\Omega} u \, dx = m \right\},$$

where $|\Omega|$ denotes the size of Ω .

The two different monomer units are represented by $u = -1$ and $u = 1$ respectively. The connectivity of the two monomer units leads to the long range interaction term $\frac{\sigma}{2} |(-\Delta)^{-1/2}(u - m)|^2$ in the free energy. Here $-\Delta$ is viewed as a positive operator, and $(-\Delta)^{-1/2}$ is the square root of its inverse. The parameter σ is proportional to the inverse of the square root of the total chain length of the copolymer. $\frac{\epsilon^2}{2} |\nabla u|^2$ represents the interfacial energy density at bonding points. The parameter ϵ is proportional to the thickness of interfaces between the two monomers. m stands for the average volume density of one of the two monomer units. It must be in the interval $(-1, 1)$.

When this free energy is minimized, the three terms of the integrand (the energy density of the material) have different preferences. The first term likes large blocks of monomers, thereby reducing the combined size of interfaces between the two monomers. The function W in the second term is a double well potential with two global minima at -1 and 1 , reflecting its preference for segregated monomers over mixtures. The third term is most interesting to us, which depends on u nonlocally, through a global operator $(-\Delta)^{-1/2}$. Hence we call F a nonlocal variational problem. The third term favours rapid oscillation between the two monomer. As these tendencies compete and compromise, small blocks rich with one of the two monomers appear. This phenomenon is known as micro-phase separation.

Equilibria of F are critical points of (1.1), or solutions to its Euler-Lagrange equation:

$$-\epsilon^2 \Delta u + f(u) + \sigma (-\Delta)^{-1}(u - m) = \lambda \text{ in } \Omega, \quad \frac{\partial u}{\partial \nu} = 0 \text{ on } \partial \Omega.$$

Here $f = W'$, and λ is a Lagrange multiplier. $(-\Delta)^{-1}(u - m)$ denotes the solution v with the Neumann boundary condition and zero average of

$$-\Delta v = u - m \text{ in } \Omega, \quad \partial_{\nu} v = 0 \text{ on } \partial \Omega, \quad \int_{\Omega} v = 0.$$

The precise meaning of $(-\Delta)^{-1/2}$ in F is not too important for our purposes. It is the square root of the positive operator $(-\Delta)^{-1}$ from $\{w \in L^2(\Omega) : \int_{\Omega} w \, dx = 0\}$ to itself. Given $u \in X_m$, if we let $v = (-\Delta)^{-1}(u - m)$, then

$$F(u) = \int_{\Omega} \left[\frac{\epsilon^2}{2} |\nabla u|^2 + W(u) + \frac{\sigma}{2} |\nabla v|^2 \right] dx,$$

which is often a more practical formula.

In this paper we continue to study F following the work in [19, 20]. The paper [19] was concerned with the one-dimensional version of the problem, $\Omega = (0, 1)$, in the parameter range: $\sigma \sim \epsilon$. There we found a family of local minima of F . For each positive integer N , there are two local minima of F . Each of them assumes values close to -1 or 1 except on N thin interfaces. In other words the copolymer forms $N + 1$ micro-domains, separated by N transition regions of mixtures. Here the micro-domains are of size 1 and the interfaces of size ϵ . See Ohnishi et al [16] and Choksi [4] for more on the scales of micro-domains.

In [20] we studied the one-dimensional problem in the parameter range $\sigma \sim 1$. We proved that the global minima of F are periodic functions whose periods have a particular asymptotic expansion in the order of $\epsilon^{1/3}$. These results extended the earlier ones of Müller [14] for the special case $m = 0$ and $W(-u) = W(u)$. So in this parameter range the micro-domains are of size $\epsilon^{1/3}$, and the interfaces are of width ϵ .

Of course the one-dimensional problem may be trivially extended to rectangles in R^2 or R^3 , and the local and global minima obtained in one-dimension may be viewed as two or three-dimensional equilibria with parallel layers. A natural question is to study equilibria with curved interfaces.

In this paper we return to the parameter range $\epsilon \sim \sigma$ to address this issue. Taking Ω to be the unit disk D in R^2 , we look for equilibria of F that are radially symmetric. Let us introduce

$$\gamma = \frac{\sigma}{\epsilon}. \quad (1.2)$$

This γ is a fixed constant, while both ϵ and σ are small positive parameters.

Let I_ϵ be a scaled version of F : $I_\epsilon = \epsilon^{-1}F$, i.e.

$$I_\epsilon(u) = \int_D \left[\frac{\epsilon}{2} |\nabla u|^2 + \frac{1}{\epsilon} W(u) + \frac{\gamma}{2} |(-\Delta)^{-1/2}(u - m)|^2 \right] dx. \quad (1.3)$$

We remind the reader that W is a smooth non-negative function assuming global minimum value 0 at ± 1 . An example is $W(u) = (u^2 - 1)^2$. The derivative of W is denoted by f . $m \in (-1, 1)$ is a volume constraint on admissible functions u .

I_ϵ is defined in the radial function class

$$X_m^R = \left\{ u \in W^{1,2}(D) : u(x) = u(|x|), \frac{1}{|D|} \int_D u \, dx = m \right\}.$$

We seek equilibria of I_ϵ that are close to ± 1 in D , except on one or more narrow circular interfaces. They represent copolymer configurations with concentrically layered monomer micro-domains.

Equilibria with a single circular interface are often called bubble solutions. When $\sigma = 0$, F_ϵ becomes the more familiar Cahn-Hilliard problem [3]. The existence and location of bubble solutions were shown by Wei and Winter in [21]. However multiply layered radial equilibria of the type studied in this paper do not exist in the Cahn-Hilliard problem.

We will construct both bubble solutions and multiply layered equilibria of I_ϵ . The main results are contained in the following theorem.

Theorem 1.1 *For any $\gamma > 0$ defined in (1.2), there exist two equilibria of I_ϵ with one circular interface when ϵ is small. For $n \geq 2$ there exists $\gamma_0 > 0$ such that if $\gamma > \gamma_0$ there exist two equilibria of I_ϵ with n circular interfaces when ϵ is small.*

The largeness condition on γ for the existence of several layer equilibria is new. In the one-dimensional case when ϵ is small there exist equilibria (actually local minima) with any prescribed number of layers for any $\gamma > 0$ (See Theorem 1.1 of [19]). However in the higher dimensional case the curvature of layers interacts with the nonlocal effect in (1.3), and the condition on γ becomes necessary.

Our strategy is to view I_ϵ for small ϵ as a singularly perturbed variational problem. After we find the singular limit: I_0 , using the theory of Γ -convergence, we show that I_0 may be studied on a family of finite dimensional sets (See Proposition 2.3). In these sets we find strict local minima of I_0 . They persist in the perturbed problem I_ϵ .

We also study a dynamic law of the free energy F . We address the issue of interface disappearance. By studying a free boundary problem, we explain how interfaces may move to the origin and vanish, or collapse to each other.

Our paper is organized as follows: Section 2 identifies the singular limit I_0 of I_ϵ ; in Section 3 we solve I_0 and prove Theorem 1.1; Section 4 studies interface disappearance; a few remarks are included in Section 5.

2 Reduction by Γ -convergence

As illustrated in [19] when ϵ is small the study of I_ϵ can sometimes be reduced to its singular limit, known as the Γ -limit of I_ϵ . It takes the form

$$I_0(u) = c_0 |Du|(D) + \frac{\gamma}{2} \int_D |(-\Delta)^{-1/2}(u - m)|^2 dx \quad (2.1)$$

where

$$c_0 = \frac{\sqrt{2}}{2} \int_{-1}^1 \sqrt{W(s)} ds.$$

I_0 is defined on the set

$$X_{0,m}^R = \{u \in L^2(D) : u(x) = u(|x|), \frac{1}{|D|} \int_D u dx = m\}, \quad (2.2)$$

although it has finite values only on a subset

$$A = \{u \in X_{0,m}^R : u \in BV(D), u(x) = \pm 1 \text{ a.e.}, \}. \quad (2.3)$$

$BV(D)$ is the space of functions on D of bounded variation. On $X_{0,m}^R \setminus A$, $I_0 = \infty$. For $u \in A$ $I_0(u)$ is defined by (2.1).

In our two-dimensional case $|Du|(D)$ in (2.1) is twice the total length of the curves separating $\{x \in D : u(x) = -1\}$ from $\{x \in D : u(x) = 1\}$. More formally we view $|Du|$ as a finite measure and denote the size of D under this measure by $|Du|(D)$. See Chapter 5 of [7] for more information on BV functions.

The general theory of Γ -convergence was developed by De Giorgi in [6]. A more complete introduction to this theory may be found in [5]. In the Cahn-Hilliard problem, i.e. $\gamma = 0$ in (1.3), this theory has been successfully applied by Modica and Mortola [13], Modica [12], Kohn and Sternberg [10]. The concept of Γ -convergence is defined by the two statements of the following proposition, which I_ϵ satisfies.

Proposition 2.1 1. For every family $\{u_\epsilon\} \subset X_m^R$ with $\lim_{\epsilon \rightarrow 0} \|u_\epsilon - u\|_2 = 0$,

$$\liminf_{\epsilon \rightarrow 0} I_\epsilon(u_\epsilon) \geq I_0(u);$$

2. For every $u \in A$, there exists a family $\{u_\epsilon\} \subset X_m^R$ such that $\lim_{\epsilon \rightarrow 0} \|u_\epsilon - u\|_2 = 0$, and

$$\limsup_{\epsilon \rightarrow 0} I_\epsilon(u_\epsilon) \leq I_0(u).$$

The primary topology of $X_{0,m}^R$ is given by the L^2 norm, denoted by $\|\cdot\|_2$. Only one property of the Γ convergence of I_ϵ to I_0 is needed for our purposes. It asserts that near every strict local minimum of I_0 there exists a local minimum of I_ϵ when ϵ is small. Denote the open ball in $X_{0,m}^R$, under the L^2 -norm, centered at u_0 of radius δ by $B_\delta(u_0)$.

Proposition 2.2 Let $\delta > 0$ and $u_0 \in A$ be such that $I_0(u_0) < I_0(u)$ for all $u \in B_\delta(u_0)$ with $u \neq u_0$. Then there exists $\epsilon_0 > 0$ such that for all $\epsilon < \epsilon_0$ there exists $u_\epsilon \in B_{\delta/2}(u_0)$ with $I_\epsilon(u_\epsilon) \leq I_\epsilon(u)$ for all $u \in B_{\delta/2}(u_0)$. In addition $\lim_{\epsilon \rightarrow 0} \|u_\epsilon - u_0\|_2 = 0$.

The proofs of these two propositions are standard and may be found in Section 2 of [19].

Every $u \in A$ may be identified by the circular interfaces where u jumps between -1 and 1 . Since the total measure $|Du|(D)$ is finite, there are finitely or countably infinitely many interfaces. If u has infinitely many interfaces, they must converge to the origin. A is naturally divided into two disjoint subsets A^- and A^+ . Every u in A^- is equal to -1 outside the largest circular interface, and every u in A^+ is equal to 1 , outside the largest circular interface.

If we denote the radii of the circular interfaces of $u \in A^\pm$ by $r_1, r_2, \dots, r_k, \dots$ in the descending order, i.e. $1 > r_1 > r_2 > \dots > r_k > \dots$, then A^\pm may be identified by

$$A^\pm = \{(r_1, r_2, \dots) : 1 > r_1 > r_2 > \dots \geq 0, r_1^2 - r_2^2 + r_3^2 - \dots = \frac{1 \mp m}{2}\}. \quad (2.4)$$

The constraint here follows directly from the constraint $\frac{1}{|\Omega|} \int_\Omega u \, dx = m$.

Members in A with finitely many interfaces are particularly important. Define

$$A_n^\pm = \{(r_1, r_2, \dots) \in A^\pm : r_{n+1} = r_{n+2} = \dots = 0\}. \quad (2.5)$$

The r_i 's are called the r -coordinates of u .

The subsets A_n^\pm form an interesting structure in A . Both of A_1^\pm contain a single element. Each of A_n^\pm , $n \geq 2$, is open in the sense that it does not include its boundary. The boundary of A_2^- is the union of A_1^- and A_1^+ . The boundary of A_2^+ is also $A_1^- \cup A_1^+$. In general A_n^- and A_n^+ share the same boundary: $\cup_{m < n} (A_m^- \cup A_m^+)$.

After factoring out a constant $\gamma\pi$, we decompose I_0 into a local part and a nonlocal part:

$$I_0(u) = \gamma\pi(L(u) + N(u)) \quad (2.6)$$

with

$$L(u) = c \sum_{k=1}^{\infty} r_k, \quad N(u) = \int_0^1 (v')^2 r \, dr.$$

Here $v = (-\Delta)^{-1}(u - m)$ and

$$c = \frac{4c_0}{\gamma} = \frac{2\sqrt{2}}{\gamma} \int_{-1}^1 \sqrt{W(s)} \, ds. \quad (2.7)$$

When using the r -coordinate system, I_0 may be expressed as a function of r_1, r_2, r_3, \dots . Let us do this for $u \in A^-$. I_0 in A^+ may be calculated in a similar way and we leave the details to the reader.

Solving the equation for v , corresponding to u , we find that on each (r_i, r_{i-1})

$$v' = \frac{c_i}{r} - \frac{(\pm 1 - m)r}{2}.$$

The c_i 's are determined by $v'(0) = v'(1) = 0$ and the continuity of v' at r_i :

$$c_1 = -\frac{1+m}{2}, \quad c_i = r_1^2 - r_2^2 + \dots + (-1)^i r_{i-1}^2 - \frac{1+m}{2}, \quad (i = 2, 3, \dots)$$

To see the expression for $I_0(u)$ in terms of the r_i 's, we note that on (r_i, r_{i-1})

$$\begin{aligned} \int_{r_i}^{r_{i-1}} (v')^2 r \, dr &= c_i^2 \log \frac{r_{i-1}}{r_i} - \frac{c_i((-1)^i - m)}{2} (r_{i-1}^2 - r_i^2) \\ &\quad + \frac{((-1)^i - m)^2}{16} (r_{i-1}^4 - r_i^4), \end{aligned}$$

which leads to

$$\begin{aligned} I_0(u) &= \gamma\pi \sum_{i=1}^{\infty} \left\{ c r_i + \left[\sum_{j=1}^{i-1} (-1)^{j-1} r_j^2 - \frac{1+m}{2} \right]^2 \log \frac{r_{i-1}}{r_i} \right. \\ &\quad - \frac{\left[\sum_{j=1}^{i-1} (-1)^{j-1} r_j^2 - \frac{1+m}{2} \right] ((-1)^i - m)}{2} (r_{i-1}^2 - r_i^2) \\ &\quad \left. + \frac{((-1)^i - m)^2}{16} (r_{i-1}^4 - r_i^4) \right\}. \quad (2.8) \end{aligned}$$

We call this expression $I_0(u)$ under the r -coordinate system. If $u \in A_n^-$, the sum becomes a finite one from 1 to $n + 1$, with $r_{n+1} = 0$.

It is often more convenient to use a different coordinate system for $u \in A^-$ (The case of $u \in A^+$ may be handled similarly):

$$y_i = \sum_{j=1}^i (-1)^{j-1} r_j^2 = r_1^2 - r_2^2 + \dots + (-1)^{i-1} r_i^2,$$

which we call the y -coordinates.

When u has only finitely many interfaces, say $u \in A_n^-$,

$$y_n = y_{n+1} = y_{n+2} = \dots = \frac{1+m}{2}.$$

So one advantage that the y -coordinate system enjoys over the r -coordinate system is that the $n - 1$ degrees of freedom of A_n^- are all reflected in the first $n - 1$ y_i 's, without the need for a constraint as in (2.4).

The condition $r_1 > r_2 > r_3 \dots$ translates to

$$1 = y_{-1} > y_1 > y_3 > y_5 > \dots > \frac{1+m}{2} > \dots > y_6 > y_4 > y_2 > y_0 = 0, \quad (2.9)$$

for y_i with $i \leq n - 1$ if $u \in A_n^-$, or with i an arbitrary positive integer if $u \in A^- \setminus A_n^-$. Note that

$$c_i = y_{i-1} - \frac{1+m}{2}, \quad r_i^2 = (-1)^{i-1} (y_i - y_{i-1}).$$

Topologically the domain (2.9) of the y_i 's is a diffeomorphism of A_n^- under the r -coordinates.

We may rewrite (2.8) under the y -coordinate system as

$$\begin{aligned} I_0(u) &= \gamma\pi \sum_{i=1}^{\infty} \left\{ c\sqrt{|y_i - y_{i-1}|} + \frac{(y_{i-1} - \frac{1+m}{2})^2}{2} \log \frac{y_{i-2} - y_{i-1}}{y_i - y_{i-1}} \right. \\ &\quad + \frac{1 - (-1)^i m}{2} (y_{i-1} - \frac{1+m}{2})(y_{i-2} - y_i) \\ &\quad \left. + \frac{[(-1)^i - m]^2}{16} (y_{i-2}^2 - 2y_{i-2}y_{i-1} + 2y_{i-1}y_i - y_i^2) \right\}. \quad (2.10) \end{aligned}$$

We remind the reader that $y_0 = 0$ and $y_{-1} = -1$ by our convention. Again when $u \in A_n^-$, this sum becomes a finite one from 1 to $n + 1$ with $y_n = y_{n+1} = \frac{1+m}{2}$.

We close this section with an important proposition which allows us to seek local minima of I_0 in the finite dimensional sets A_n^\pm .

Proposition 2.3 *If u is a strict local minimum of I_0 in A_n^- , or A_n^+ for some $n \geq 1$, then u is also a strict local minimum of I_0 in $X_{0,m}^R$.*

Proof. Suppose that u is a strict local minimum of I_0 in A_n^- . Since $I_0 = \infty$ outside A , it suffices to show that u is a strict local minimum in A .

We do so by contradiction. Assume that there exists a sequence $u_k \in A$ such that $\|u_k - u\|_2 \rightarrow 0$ and $I_0(u_k) \leq I_0(u)$.

Let us denote the radii of interfaces of u_k by $r_1^k, r_2^k, r_3^k, \dots$, and the radii of the interfaces of u by r_1, r_2, \dots, r_n . By the L^2 continuity of N in $X_{0,m}^R$, $N(u_k) \rightarrow N(u)$. To accommodate both $I_0(u_k) \leq I_0(u)$ and $\|u_k - u\|_2 \rightarrow 0$ we must have

$$\lim_{k \rightarrow \infty} r_j^k = r_j, \quad j = 1, 2, \dots, n, \quad \lim_{k \rightarrow \infty} \sum_{j=n+1}^{\infty} r_j^k = 0, \quad j = n+1, n+2, \dots$$

The condition $\|u_k - u\|_2 \rightarrow 0$ also implies

$$\lim_{k \rightarrow \infty} \sum_{j=1}^{\infty} [(r_{n+2j-1}^k)^2 - (r_{n+2j}^k)^2] = 0.$$

They imply that in the y -coordinates

$$\lim_{k \rightarrow \infty} y_j^k = y_j, \quad j = 1, 2, \dots, n-1, \quad \lim_{k \rightarrow \infty} y_j^k = \frac{1+m}{2}, \quad j = n, n+2, \dots \quad (2.11)$$

uniformly in j . Here y_j^k , $j = 1, 2, 3, \dots$, are the y -coordinates of u_k , and y_j , $j = 1, 2, \dots, n-1$, the y -coordinates of u .

Next we define $w_k \in A_n^-$, with y -coordinates $(y_1^k, y_2^k, \dots, y_{n-1}^k, \frac{1+m}{2}, \frac{1+m}{2}, \dots)$. Of the n interfaces that w_k has the first $n-1$ are shared with those of u_k . The n -th one of w_k is slightly different from that of u_k . Clearly $\|w_k - u\|_2 \rightarrow 0$. We show that $I_0(u_k) \geq I_0(w_k)$. Break $\frac{1}{\gamma\pi}(I_0(u_k) - I_0(w_k))$ into three parts: T_1 , T_2 , and T_3 , where

$$\begin{aligned} T_1 &= \sum_{i=n+2}^{\infty} \left\{ c\sqrt{|y_i^k - y_{i-1}^k|} + \frac{(y_{i-1}^k - \frac{1+m}{2})^2}{2} \log \frac{y_{i-2}^k - y_{i-1}^k}{y_i^k - y_{i-1}^k} \right. \\ &\quad + \frac{1 - (-1)^i m}{2} (y_{i-1}^k - \frac{1+m}{2})(y_{i-2}^k - y_i^k) \\ &\quad \left. + \frac{((-1)^i - m)^2}{16} ((y_{i-2}^k)^2 - 2y_{i-2}^k y_{i-1}^k + 2y_{i-1}^k y_i^k - (y_i^k)^2) \right\}, \\ T_2 &= \left\{ c\sqrt{|y_{n+1}^k - y_n^k|} + \frac{(y_n^k - \frac{1+m}{2})^2}{2} \log \frac{y_{n-1}^k - y_n^k}{y_{n+1}^k - y_n^k} \right. \\ &\quad + \frac{1 - (-1)^{n+1} m}{2} (y_n^k - \frac{1+m}{2})(y_{n-1}^k - y_{n+1}^k) \\ &\quad + \frac{((-1)^{n+1} - m)^2}{16} ((y_{n-1}^k)^2 - 2y_{n-1}^k y_n^k + 2y_n^k y_{n+1}^k - (y_{n+1}^k)^2) \left. \right\} \\ &\quad - \frac{((-1)^{n+1} - m)^2}{16} (y_{n-1}^k - \frac{1+m}{2})^2, \\ T_3 &= \left\{ c\sqrt{|y_n^k - y_{n-1}^k|} + \frac{(y_{n-1}^k - \frac{1+m}{2})^2}{2} \log \frac{y_{n-2}^k - y_{n-1}^k}{y_n^k - y_{n-1}^k} \right. \end{aligned}$$

$$\begin{aligned}
& + \frac{1 - (-1)^n m}{2} (y_{n-1}^k - \frac{1+m}{2}) (y_{n-2}^k - y_n^k) \\
& + \frac{((-1)^n - m)^2}{16} ((y_{n-2}^k)^2 - 2y_{n-2}^k y_{n-1}^k + 2y_{n-1}^k y_n^k - (y_n^k)^2) \} \\
& - \{ c \sqrt{|\frac{1+m}{2} - y_{n-1}^k|} + \frac{(y_{n-1}^k - \frac{1+m}{2})^2}{2} \log \frac{y_{n-2}^k - y_{n-1}^k}{\frac{1+m}{2} - y_{n-1}^k} \\
& + \frac{1 - (-1)^n m}{2} (y_{n-1}^k - \frac{1+m}{2}) (y_{n-2}^k - \frac{1+m}{2}) \\
& + \frac{((-1)^n - m)^2}{16} ((y_{n-2}^k)^2 - 2y_{n-2}^k y_{n-1}^k + 2y_{n-1}^k (\frac{1+m}{2}) - (\frac{1+m}{2})^2) \}.
\end{aligned}$$

According to the computation leading to (2.8-2.10) each term in the sum of T_1 is simply

$$c r_i^k + \int_{r_i^k}^{r_{i-1}^k} (v'_k)^2 r \, dr \geq 0,$$

where $v'_k = (-\Delta)^{-1}(u_k - m)$. Hence $T_1 \geq 0$.

We rewrite T_2 as

$$\begin{aligned}
T_2 &= c \sqrt{|y_{n+1}^k - y_n^k|} + \frac{(y_n^k - \frac{1+m}{2})^2}{2} \log \frac{y_{n-1}^k - y_n^k}{y_{n+1}^k - y_n^k} \\
&+ \frac{1 - (-1)^{n+1} m}{2} (y_n^k - \frac{1+m}{2}) (y_{n-1}^k - y_{n+1}^k) + \frac{((-1)^{n+1} - m)^2}{2} \\
&\cdot [-2y_{n-1}^k (y_n^k - \frac{1+m}{2}) + 2y_n^k y_{n+1}^k - (y_{n+1}^k)^2 - (\frac{1+m}{2})^2].
\end{aligned}$$

Since $|y_n^k - \frac{1+m}{2}| < |y_{n+1}^k - y_n^k|$, we may bound the last three terms below by $-C_1 |(y_{n+1}^k - y_n^k) \log(y_{n+1}^k - y_n^k)|$, which is in turn controlled by the first term. For the sake of the next estimate, we save half of the first term and deduce that for large k

$$\begin{aligned}
T_2 &\geq c \sqrt{|y_{n+1}^k - y_n^k|} - C_1 |(y_{n+1}^k - y_n^k) \log(y_{n+1}^k - y_n^k)| \\
&\geq \frac{c}{2} \sqrt{|y_{n+1}^k - y_n^k|}.
\end{aligned} \tag{2.12}$$

For T_3 we note that

$$(y_{n-1}^k - \frac{1+m}{2})(y_{n-2}^k - y_n^k) - (y_{n-1}^k - \frac{1+m}{2})(y_{n-2}^k - \frac{1+m}{2}) \geq 0$$

by (2.9). This yields

$$\begin{aligned}
T_3 &\geq c (\sqrt{|y_n^k - y_{n-1}^k|} - \sqrt{|\frac{1+m}{2} - y_{n-1}^k|}) \\
&+ \frac{(y_{n-1}^k - \frac{1+m}{2})^2}{2} [\log |\frac{1+m}{2} - y_{n-1}^k| - \log |y_n^k - y_{n-1}^k|] \\
&+ \frac{((-1)^n - m)^2}{16} [2y_{n-1}^k - y_n^k - \frac{1+m}{2}] (y_n^k - \frac{1+m}{2}).
\end{aligned}$$

Since both $y_{n-1}^k - y_n^k$ and $y_{n-1}^k - \frac{1+m}{2} \rightarrow y_{n-1} - \frac{1+m}{2} \neq 0$, the mean value theorem is applied to the square root and logarithmic functions to conclude that T_3 is bounded below by $-C_2|y_n^k - \frac{1+m}{2}|$. Again by (2.9) $|y_n^k - \frac{1+m}{2}| < |y_n^k - y_{n+1}^k|$, so we use what we have saved in (2.12) to conclude that as $|y_{n+1}^k - y_n^k| \rightarrow 0$,

$$T_2 + T_3 \geq \frac{c}{2} \sqrt{|y_{n+1}^k - y_n^k|} - C_2|y_{n+1}^k - y_n^k| \geq 0.$$

Once having proved $I_0(u_k) \geq I_0(w_k)$, we recall that u is a strict local minimum in A_n^- and $w_k \in A_n^-$ approaches u . So $I_0(u_k) > I_0(u)$, contradicting the assumption at the start of the proof. \square

3 Local minima of I_0 in A_n^\pm

Proposition 2.3 suggests that we seek local minima of I_0 in A_n^\pm . We do so in this section. Recall that for elements in A_n^\pm , only their y_1, y_2, \dots, y_{n-1} coordinates are variables, and $y_n = y_{n+1} = \dots = \frac{1+m}{2}$ are constants. It is convenient to introduce

$$p_i = 1 - (-1)^i m. \quad (3.1)$$

The nonlocal part N of I_0 , defined in (2.6), is the focus of this section.

Proposition 3.1 *In each A_n^\pm N has a unique critical point $(y_1, y_2, \dots, y_{n-1})$ which satisfies*

$$p_0 y_n > p_1(y_1 - y_n) > p_2(y_2 - y_1) > \dots > (-1)^{n-1} p_{n-1}(y_n - y_{n-1}) > 0.$$

Proof. In each of A_1^\pm there is only one element, which is considered trivially a critical point.

In A_n^- ($n \geq 2$) the derivatives of N with respect to the y_i 's are

$$\begin{aligned} \frac{\partial N}{\partial y_1} &= \frac{p_2(-y_2)}{2} + (y_1 - y_n) \log \frac{-y_1}{y_2 - y_1}, \\ \frac{\partial N}{\partial y_i} &= \frac{p_{i+1}(y_{i-1} - y_{i+1})}{2} + (y_i - y_n) \log \frac{y_{i-1} - y_i}{y_{i+1} - y_i}, \\ \frac{\partial N}{\partial y_{n-1}} &= \frac{p_n(y_{n-2} - y_n)}{2} + (y_{n-1} - y_n) \log \frac{y_{n-2} - y_{n-1}}{y_n - y_{n-1}}. \end{aligned}$$

If $(y_1, y_2, \dots, y_{n-1})$ is a critical point, set

$$z_{n-1} = \frac{y_{n-2} - y_n}{y_n - y_{n-1}} > 0. \quad (3.2)$$

Then $\frac{\partial N}{\partial y_{n-1}} = 0$ implies

$$\frac{p_n}{2} z_{n-1} = \log(1 + z_{n-1}) \quad (3.3)$$

which is solvable for $z_{n-1} > 0$ if and only if $\frac{p_n}{2} < 1$, and it is true since $m \in (-1, 1)$. So there exists a unique z_{n-1} solely determined by (3.3). It depends on m only.

Next we let

$$z_{n-2} = \frac{y_{n-3} - y_{n-1}}{y_{n-1} - y_{n-2}} > 0. \quad (3.4)$$

The condition $\frac{\partial N}{\partial y_{n-2}} = 0$ implies

$$\frac{p_{n-1}}{2} \frac{y_{n-1} - y_{n-2}}{y_n - y_{n-2}} z_{n-2} = \log(1 + z_{n-2}). \quad (3.5)$$

By (3.2) it is z_{n-1} rather than y_{n-1} and y_{n-2} that determines this equation. To have a positive solution of z_{n-2} we must have $\frac{p_{n-1}}{2} \frac{y_{n-1} - y_{n-2}}{y_n - y_{n-2}} < 1$, or equivalently

$$\frac{p_{n-1}(y_{n-1} - y_n)}{p_{n-2}(y_n - y_{n-2})} < 1. \quad (3.6)$$

Because of (3.2), (3.6) is indeed a requirement solely on z_{n-1} : $z_{n-1} > \frac{p_{n-1}}{p_{n-2}}$. To verify this condition, we recall the equation (3.3) that determines z_{n-1} . We must have

$$\frac{p_n}{2} \frac{p_{n-1}}{p_{n-2}} < \log\left(1 + \frac{p_{n-1}}{p_{n-2}}\right),$$

or equivalently

$$\log\left(1 - \frac{p_{n-1}}{2}\right) < -\frac{p_{n-1}}{2},$$

which is true since $p_{n-1} \neq 0$. Thus we have obtained a unique z_{n-2} , determined from (3.5), depending on m and z_{n-1} only.

In order to facilitate induction, we show that

$$\frac{p_{n-2}(y_{n-2} - y_n)}{p_{n-3}(y_n - y_{n-3})} < 1, \quad (3.7)$$

which by (3.2) and (3.4) is a requirement on z_{n-1} and z_{n-2} . After eliminating y_{n-3} by (3.4) we turn (3.7) to

$$z_{n-2} > \frac{p_{n-2}(y_{n-2} - y_n) + p_{n-1}(y_{n-1} - y_n)}{p_{n-1}(y_{n-2} - y_{n-1})}.$$

This is satisfied if, according to (3.5),

$$\begin{aligned} & \frac{p_{n-1}}{2} \frac{p_{n-2}(y_{n-2} - y_n) + p_{n-1}(y_{n-1} - y_n)}{p_{n-1}(y_{n-2} - y_{n-1})} \\ & < \log\left(1 + \frac{p_{n-2}(y_{n-2} - y_n) + p_{n-1}(y_{n-1} - y_n)}{p_{n-1}(y_{n-2} - y_{n-1})}\right). \end{aligned}$$

This simplifies to

$$\begin{aligned} & \log\left(1 + \frac{p_{n-1}(y_n - y_{n-1}) + p_{n-2}(y_n - y_{n-2})}{2(y_{n-2} - y_n)}\right) \\ & < \frac{p_{n-1}(y_n - y_{n-1}) + p_{n-2}(y_n - y_{n-2})}{2(y_{n-2} - y_n)}, \end{aligned}$$

Note that at a critical point

$$\begin{aligned}
\frac{\partial^2 N}{\partial y_i^2} &= \frac{p_{i+1}(y_{i+1} - y_{i-1})}{2(y_i - y_n)} + \frac{y_i - y_n}{y_i - y_{i-1}} - \frac{y_i - y_n}{y_i - y_{i+1}} \\
&= \frac{-p_i(y_i - y_n) + p_{i-1}(y_n - y_{i-1})}{2(y_i - y_{i-1})} \cdot \frac{y_n - y_{i-1}}{y_i - y_n} \\
&\quad + \frac{p_i(y_i - y_n) - p_{i+1}(y_n - y_{i+1})}{2(y_i - y_{i+1})} \cdot \frac{y_n - y_{i+1}}{y_i - y_n}
\end{aligned} \tag{3.11}$$

Take a vector $\vec{h} = (h_1, \dots, h_{n-1})$ and consider the quadratic form

$$\begin{aligned}
&\sum_{i,j=1}^{n-1} \frac{\partial^2 N}{\partial y_i \partial y_j} h_i h_j \\
&= \sum_{j=1}^{n-1} \frac{\partial^2 N}{\partial y_j^2} h_j^2 + 2 \sum_{j=2}^{n-1} \frac{\partial^2 N}{\partial y_j \partial y_{j-1}} h_j h_{j-1} \\
&= \sum_{i=2}^{n-1} \frac{-p_i(y_i - y_n) + p_{i-1}(y_n - y_{i-1})}{2(y_i - y_{i-1})} \left(\sqrt{\frac{y_n - y_{i-1}}{y_i - y_n}} h_{i-1} - \sqrt{\frac{y_i - y_n}{y_n - y_{i-1}}} h_i \right)^2 \\
&\quad + \frac{-p_1(y_1 - y_n) + p_0 y_n}{2y_1} \cdot \frac{y_n}{y_1 - y_n} h_1^2
\end{aligned}$$

by (3.11). This quantity is positive when $\vec{h} \neq \vec{0}$ by the inequalities in Proposition 3.1. Thus N is positive definite at the critical point. \square

Proposition 3.3 *The lone members in A_1^\pm are local minima of I_0 for any positive γ . In A_n^\pm , $n \geq 2$, I_0 has a strict local minimum if γ is large.*

Proof. The lone elements in A_1^\pm are considered minima for any $\gamma > 0$. In A_n^\pm ($n \geq 2$), the proposition follows from Propositions 3.1 and 3.2, since non-degenerate local minima of N persist under perturbation to $L + N$ when c is small, i.e. γ is large. \square

The largeness condition in this proposition can not be removed. For instance in A_2^- with $m = 0$,

$$\frac{1}{\gamma\pi} \frac{\partial I_0}{\partial y_1} = \frac{c}{2} \left(\frac{1}{\sqrt{y_1}} + \frac{1}{\sqrt{y_1 - 0.5}} \right) - \frac{1}{4} + (y_1 - 0.5) \log \frac{-y_1}{0.5 - y_1}$$

is positive in $(0.5, 1)$ if c is large, i.e. γ is small. Then there is no local minimum. In general the local part L of I_0 is concave in A_n^\pm , because

$$\sum_{i,j=1}^{n-1} \frac{\partial^2 L}{\partial y_i \partial y_j} h_i h_j = -\frac{c}{4} \left[\sum_{i=2}^{n-1} |y_i - y_{i-1}|^{-\frac{3}{2}} (h_i - h_{i-1})^2 + y_1^{-\frac{3}{2}} h_1^2 + |y_{n-1} - y_n|^{-\frac{3}{2}} h_{n-1}^2 \right]$$

is negative if $(h_1, h_2, \dots, h_{n-1}) \neq \vec{0}$. Then I_0 is concave if γ is small. Since A_n^\pm do not include their boundaries (The boundaries of A_n^\pm consist of A_m^\pm , $m < n$), there is no local minimum in A_n^\pm .

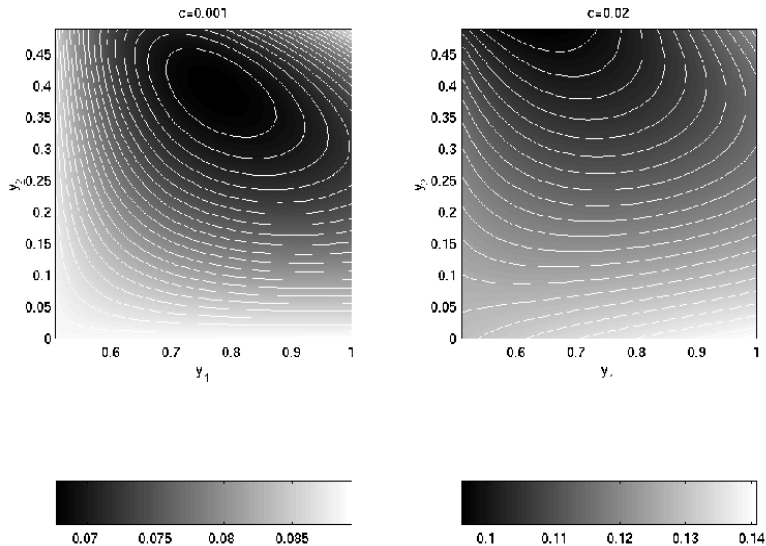


Figure 1: Contour maps of $\frac{1}{\gamma\pi}I_0$ in A_3^{-1} .

In A_3^- , with $m = 0$, the two plots in Figure 1 give the contour maps of $\frac{1}{\gamma\pi}I_0$ when γ is large, where there is a local minimum, and when γ is small, where there is no local minimum.

Although N has only one critical point in each A_n^\pm , I_0 may have more. In A_2^- , when γ is large, I_0 has a local maximum before the local minimum, mentioned in Proposition 3.3. The first plot of Figure 2 shows the graph of $\frac{1}{\gamma\pi}I_0$ vs. y_1 with a large γ , and the second plot enlarges a portion of this picture so we can see a local maximum followed by a local minimum. On the contrary in the one-dimensional case $\Omega = (0, 1)$, the Γ limit has a unique critical point, which is a local minimum in each set of functions with n jumps (See [19]).

We remark at this point that if we study the Cahn-Hilliard problem in the current setting, there is no local minimum of the corresponding Γ -limit in any A_n^\pm , $n \geq 2$, simply because of the absence of N and the concavity of L .

Proof of Theorem 1.1. This follows immediately from Propositions 2.2, 2.3 and 3.3. \square

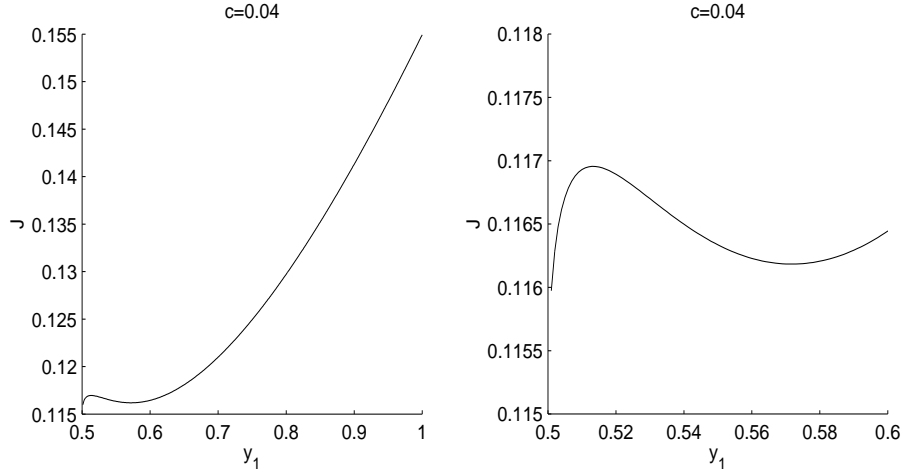


Figure 2: Graph of $\frac{1}{\gamma\pi}I_0$ in A_2^{-1} .

4 Layer disappearance

We turn our attention to the dynamics of the copolymer problem.

A simple dynamic law of F , (1.1), is the fourth order partial differential equation

$$\epsilon u_t = \Delta(-\epsilon^2 \Delta u + f(u)) - \sigma(u - m) \quad (4.1)$$

under the boundary conditions

$$\frac{\partial u}{\partial \nu} \Big|_{\partial \Omega} = \frac{\partial \Delta u}{\partial \nu} \Big|_{\partial \Omega} = 0. \quad (4.2)$$

This is a diffusive model where diffusion is driven by the the chemical force from the free energy F . It ignores the kinetics of motion.

In the asymptotic regime $\sigma \sim \epsilon$ where we have the Γ -limit (2.1), there is a corresponding dynamic singular limit, identified by Nishiura and Ohmishi in [15]. It is a free boundary problem (FBP) which generalizes the one associated with the Cahn-Hilliard problem (see e.g. Pego [18]). Suppose that S is the set of interfaces separating Ω into Ω^- where $u = -1$ and Ω^+ where $u = 1$. Then it evolves under the following law:

$$\Delta h = 0 \quad \text{in } \Omega^\pm \quad (4.3)$$

$$\frac{\partial h}{\partial \nu} = 0 \quad \text{on } \partial \Omega \quad (4.4)$$

$$V = -\frac{1}{2} \left[\frac{\partial h}{\partial \nu} \right] \quad \text{on } S \quad (4.5)$$

$$\frac{cK}{4} = h - (-\Delta)^{-1}(u - m) \quad \text{on } S, \quad (4.6)$$

where V is the normal velocity, K the mean curvature of S , and c the same constant (2.7). The normal direction ν of S in (4.5) is towards Ω^+ . [...] there denotes the jump of the directional derivative. V is positive if motion is in the same direction. The curvature is counted positive if the center of curvature lies on the Ω^+ side.

The convergence of (4.1-4.2) to (4.3-4.6) in the class of radial functions was shown in Henry [9].

Applied to the the radially symmetric case I_0 in A_n^- , the FBP takes a simpler form: when the radii of the interfaces are denoted by r_1, r_2, \dots, r_n , they satisfy a system of differential equations

$$\begin{aligned} \frac{dr_i}{dt} = & \frac{-\frac{c}{4}\left(\frac{1}{r_{i-1}} + \frac{1}{r_i}\right) - (-1)^i[v(r_{i-1}) - v(r_i)]}{2r_i \log \frac{r_i}{r_{i-1}}} \\ & + \frac{-\frac{c}{4}\left(\frac{1}{r_{i+1}} + \frac{1}{r_i}\right) + (-1)^i[v(r_i) - v(r_{i+1})]}{2r_i \log \frac{r_i}{r_{i+1}}}, \end{aligned} \quad (4.7)$$

where $v = (-\Delta)^{-1}(u - m)$. When $i = 1$ the first term on the right side of (4.7) is absent, and when $i = n$ the second term is absent. With respect to y -coordinates, the system (4.7) becomes

$$\begin{aligned} \frac{dy_i}{dt} = & -\frac{\frac{(-1)^{i-1}c}{2\sqrt{|y_{i-1}-y_i|}} + \frac{(-1)^{i+1}c}{2\sqrt{|y_{i+1}-y_i|}} + \frac{p_{i+1}(y_{i-1}-y_{i+1})}{2} + (y_i - y_n) \log \frac{y_{i-1}-y_i}{y_{i+1}-y_i}}{\log \frac{y_{i-1}-y_i}{y_{i+1}-y_i}} \\ = & -\frac{1}{\gamma\pi \log \frac{y_{i-1}-y_i}{y_{i+1}-y_i}} \cdot \frac{\partial I_0}{\partial y_i}, \end{aligned} \quad (4.8)$$

for $i = 1, 2, \dots, n-1$.

Along a solution $y_i(t)$ of (4.8)

$$\frac{dI_0}{dt} = -\sum_{i=1}^{n-1} \frac{1}{\gamma\pi \log \frac{y_{i-1}-y_i}{y_{i+1}-y_i}} \cdot \left(\frac{\partial I_0}{\partial y_i}\right)^2.$$

The log terms are all positive by (2.9), so I_0 is a Lyapunov functional of (4.8).

Several issues including interface disappearance may be addressed by the properties of I_0 .

Convergence to the equilibria. Take an initial configuration $u \in A_2^-$. u has two circular interfaces r_1 and r_2 . If u is close to the local minimum of I_0 , depicted in Figure 2, then under the FBP u converges to this local minimum. Same convergence results hold for the local minima of I_0 in other A_n^\pm .

Disappearance at the origin. However if we take the initial $u \in A_2^-$ in such a way that r_1 of u is slightly smaller than the r_1 -coordinate of the local maximum in Figure 2, then r_1 moves towards $\frac{1+m}{2}$ and r_2 towards 0. This way the inner

interface r_2 shrinks to 0 and disappears. In other words u in A_2^- moves to a boundary point of A_2^- , which is the lone element of A_1^- .

Here we make a note that according to Fife and Hillhorst [8] interfaces do not disappear or emerge in the FBP when $\Omega = (0, 1)$, due to the absence of the curvature term in (4.6).

The local maximum of I_0 in A_2^- depicted in Figure 2 is a saddle point of I_0 in A . We speculate that it also corresponds to a saddle point of I_ϵ , with a one-dimensional unstable manifold. However the Γ -convergence theory is not applicable in this situation.

More can be said from Figure 2. We note that letting $r_2 \searrow 0$ is the only way for u to leave A_2^- . Since the energy I_0 goes up as $r_1 \nearrow 1$, we can not lose the outer interface r_1 by having $r_1 \nearrow 1$. So u can not move to the second boundary point of A_2^- , which is the lone element in A_1^+ .

This type of interface disappearance may occur in other A_n^\pm as well. A initial u starting in A_n^- (or A_n^+ respectively) may move to a boundary point, which is a member in some A_m^- (or A_m^+ respectively) with $m < n$.

Interface collapsing. Another interesting question is whether the FBP may lose interfaces by collapsing some of them into each other. This actually can happen. For example we take A_3^- and consider the case that r_1, r_2 and r_3 are all close to each other. In terms of y_1 and y_2 this means $y_1 \searrow \frac{1+m}{2}$ and $y_2 \searrow 0$. Compute

$$\frac{1}{\gamma\pi} \nabla I_0(y_1 = y_3, y_2 = 0) = \left(\frac{c}{\sqrt{y_3}}, -\frac{c}{\sqrt{y_3}} \right).$$

This gradient vector and the ones nearby all point to the southwest direction. It implies that any initial u in this neighbourhood will move to the y_2 axis, causing the r_1 circle to move to $\sqrt{\frac{1+m}{2}}$ and the r_2 and r_3 circles to collapse to each other and disappear.

Nucleation. There is also the issue of nucleation. Here nucleation is the opposite of interface disappearance. Can the FBP create interfaces? In general the answer is no. This is because creating interfaces away from the origin causes I_0 to jump up, and creating interfaces near the origin, as opposite to losing interfaces, which was discussed earlier, also increases I_0 . This was essentially illustrated in the proof of Proposition 2.3.

5 Discussion

Our study of concentrically layered equilibria of I_ϵ revealed how curved interfaces behave in the di-block copolymer problem.

We first considered the static problem by seeking local minima of the free energy I_ϵ in the class of radial functions. Analyzing the singular limit I_0 of I_ϵ we constructed equilibria of I_ϵ with one circular interface when $\epsilon \sim \sigma$ are both small.

To find equilibria of I_ϵ with multiple circular interfaces we needed to impose an extra condition that $\gamma = \frac{\sigma}{\epsilon}$ is large. This contrasts with the parallel interface situation, where equilibria with multiple interfaces always exist regardless of the value of γ .

A related question is to fix a large γ and ask how many multiply layered equilibria exist and how many layers there are. To answer this question we have to study the graph of I_0 in each A_n^\pm , and find the A_n^\pm 's where I_0 has local minima. It is a quite tedious task due to the complex formula (2.8) or (2.10). We believe that there should be two positive integers $N_\gamma^\pm \geq 1$, such that if and only if $n \leq N_\gamma^-$ ($n \leq N_\gamma^+$ respectively), there is a local minimum in A_n^- (A_n^+ respectively).

When such a layered equilibrium exists, the location of the interfaces is determined by the r -coordinates of the local minimum of I_0 in A_n^\pm . Unlike the case of parallel interfaces (See [19]), the circular interfaces do not appear periodically. This suggests the role that the different curvatures ($\frac{1}{r_i}$ when the radii are r_i) of the interfaces play in this problem.

To better understand the curvature factor we turned to a dynamic law associated with the functional I_ϵ . It has a free boundary problem as a singular limit and the functional I_0 serves as a Lyapunov functional of this limit. In this dynamic problem, the curvatures of the interfaces enter the equation. In addition to the observation of convergence to the layered equilibria, we found initial elements in A that lead to interface disappearance at the origin, or interface collapsing to each other. These two phenomena contrast nicely with the case of parallel interfaces ($\Omega = (0, 1)$), where neither of them exists.

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