

Scaling Laws in Microphase Separation of Diblock Copolymers

R. Choksi

Department of Mathematics, Simon Fraser University, Burnaby, BC V5A 1S6, Canada
E-mail: choksi@math.sfu.ca

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Summary. In this note, we study a nonlocal variational problem modeling microphase separation of diblock copolymers ([22], [3], [21]). We apply certain new tools developed in [5] to determine the principal part of the asymptotic expansion of the minimum free energy. That is, we prove a scaling law for the minimum energy and confirm that it is attained by a simple periodic lamellar structure. A previous result of Ohnishi et al. [23] was for one space dimension. Here, we obtain a similar result for the full three-dimensional problem.

1. Introduction

Pattern morphology dictated by the minimization of a free energy containing a nonlocal term is well established in the context of micromagnetics and magnetic domains ([15]). Recently, new mathematical tools have been applied to gain inference behind the minimization process and properties of minimizing configurations (see [8] and the references therein). Similar energy functionals arising in domain morphology for ferrofluids and during the intermediate state of a type-1 superconductor have recently been analyzed in [24] and [6], respectively. Nonlocal effects, however, are hardly confined to magnetic behavior and the purpose of this note is to apply certain new tools, namely the use of interpolation inequalities, to microphase separation of diblock copolymers.

A diblock copolymer is a linear-chain molecule consisting of two subchains joined covalently to each other. One of the subchains is made of A monomers and the other of B monomers (see the left side of Figure 1). Below a critical temperature T_c , even a weak repulsion between unlike monomers A and B induces a strong repulsion between the subchains; thus the subchains segregate. Now consider a system of many such macromolecules. The immiscibility of these monomers drives the system to form structures that minimize contacts between the unlike monomers. This tendency to

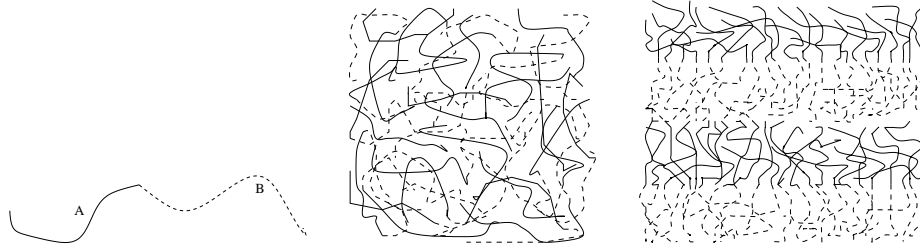


Fig. 1. (left) A diblock copolymer; (center) above T_c , the subchains mix to form a uniform disordered state, (right) below T_c , subchains tend to segregate into A-rich and B-rich regions which for the case of equal molecular weights is lamellar in structure. Here we have just shown two layers of diblock copolymers.

separate the monomers into A-rich and B-rich domains is counterbalanced by the entropy cost associated with stretching polymers so as to fill space (this is required due to the incompressibility of copolymer melts). Because of this energetic competition, macroscopic separation does not occur but rather a phase separation on a mesoscopic scale with A-rich and B-rich domains emerges. The mesoscopic domains that are observed are highly regular periodic structures; for example, when the lengths of the A and B subchains are roughly the same, a lamellar structure is observed (the right side of Figure 1). For nonequal molecular weights, a variety of periodic structures are observed from small bcc-centred spheres and circular tubes, to bicontinuous gyroids (see for example, [4], [9], [19]). These ordered structures are key to the mechanical properties that make diblock copolymers of great technological importance. Moreover, block copolymers provide simple and easily controlled materials for the study of self-assembly. Mean field theories, with an associated free energy functional, have proven very useful in the understanding and prediction of the pattern morphology ([4]). Such energy functionals consist of competing terms and, as noted by Bates and Fredrickson [4] in *Physics Today*, “minimization of the free energy for a particular geometry (compared to all other candidate geometries) indicates the most likely configuration and scale length for a block copolymer.”

In this article we analyze the microphase separation via minimization of a free energy functional proposed in [22], [3] (see [21] for precise form):

$$E_{\varepsilon,\sigma}(u) := \int_{\Omega} \varepsilon^2 |\nabla u|^2 + W(u) + \sigma \left| (-\Delta)^{-\frac{1}{2}} (u - m) \right|^2 dx, \quad (1.1)$$

where m denotes the average of u over Ω , i.e.,

$$m := \int_{\Omega} u dx.$$

In this mean field approach to the separation, u represents the local density difference of monomers A and B, i.e.,

$$u = \frac{\rho_A - \rho_B}{\rho_{total}},$$

where ρ_A and ρ_B denote the local density of A and B monomers. Hence, $u = 1$ denotes a pure A state, $u = -1$ denotes a pure B state, and an intermediate value of u signifies a mixture of the two monomers. $W(u)$ represents a double-well energy which prefers the segregated monomers (i.e., $W = 0$ iff $u = \pm 1$) to a mixture. The term $\varepsilon^2 |\nabla u|^2$ is the interfacial energy density representing energy at regions of bonding. The parameter ε is the length of this bonding region. The different subchains are all chemically bounded and the entropic penalty due to chain stretching is responsible, via a statistical physics derivation, for the nonlocal long-range interaction term (see [22], the references therein, and Remark 3.4). In this derivation one finds that the parameter σ is inversely proportional to the square of the total “chain length” \mathcal{N} of the copolymer molecule measured in terms of the total number of monomers per copolymer molecule. The parameter \mathcal{N} is often referred to as either the *polymerization index* or the *degree of polymerization*, and in practice is quite large, hence σ small. The set $\Omega \subset \mathbf{R}^3$ represents the physical space which, for convenience, is taken to be the unit cube $[0, 1]^3$. The average m measures the mass ratio of the two monomers and hence depends on the relative length of the A subchain to the B subchain of the copolymer molecule. In this article we will deal with the basic case where the lengths of the A and B subchains are equal; i.e., we use a symmetric double well potential and take $m = 0$. The assumptions we make on the material parameters are that

$$0 < \varepsilon \leq \sigma < 1. \quad (1.2)$$

In particular, our results hold for both the regime $0 < \varepsilon \ll \sigma \ll 1$ studied by Nishiura and Ohnishi in [21] appropriate for the strong segregation limit ([22]), as well as the regime $0 < \varepsilon \sim \sigma \ll 1$.

Turning to the nonlocal term, the operator $-\Delta$ is the Laplace operator with Neumann boundary conditions (zero flux). Its inverse, as an operator on the set of functions in L^2 with zero average, is self-adjoint and positive. The operator $(-\Delta)^{-\frac{1}{2}}$ denotes its unique positive square root. This way of writing the nonlocal term was chosen by Nishiura and Ohnishi because of their “Cahn-Hilliard approach” to the analysis of the variational problem (cf. [21]). In terms of the Green’s function $G(\mathbf{x}, \mathbf{y})$ for $-\Delta$ with Neumann boundary conditions, the nonlocal term can be written as

$$\sigma \int_{\Omega} \int_{\Omega} G(\mathbf{x}, \mathbf{y}) u(\mathbf{x}) u(\mathbf{y}) d\mathbf{x} d\mathbf{y}. \quad (1.3)$$

We refer the reader to Remark 3.4 for a discussion on alternate nonlocal expressions with different kernels. In this article, we will use Fourier series, and hence will write the nonlocal energy in terms of the Fourier coefficients. It will therefore be convenient, and without loss of generality, to work within the class of admissible states which also satisfy the zero flux (Neumann) boundary condition. That is, the class of admissible states \mathcal{A} is

$$\mathcal{A} := \left\{ u \in H^1(\Omega) \mid \frac{\partial u}{\partial \nu} \Big|_{\partial\Omega} = 0, \int_{\Omega} u d\mathbf{x} = 0 \right\},$$

where ν denotes the outer normal to $\partial\Omega$. We consider the Fourier series representation of u defined on Ω with coefficients $u_{\mathbf{n}}$ ($\mathbf{n} \in \mathbf{Z}^3$), i.e., the Fourier cosine series. Then

$$\int_{\Omega} \left| (-\Delta)^{-\frac{1}{2}}(u) \right|^2 d\mathbf{x} = \sum_{\mathbf{n} \in \mathbf{Z}^3} \frac{|u_{\mathbf{n}}|^2}{|\mathbf{n}|^2}. \quad (1.4)$$

Here and throughout the sequel, the sum over $\mathbf{n} \in \mathbf{Z}^3$ excludes the $\mathbf{n} = 0$ term. Note that the right-hand side of (1.4) is simply the H^{-1} norm of u ; that is, the nonlocal term in the energy is simply a negative Sobolev norm. The resulting variational problem is

$$(\mathcal{P}) \quad \min_{u \in \mathcal{A}} E_{\varepsilon, \sigma} = \int_{\Omega} \varepsilon^2 |\nabla u|^2 + W(u) + \sigma \sum_{\mathbf{n} \in \mathbf{Z}^3} \frac{|u_{\mathbf{n}}|^2}{|\mathbf{n}|^2},$$

within the parameter regime (1.2). The pattern morphology can now be explained from the competition between the three terms in the free energy. Namely, the double well potential prefers segregated monomers to a mixture. The interfacial energy penalizes interfaces between such monomers and thus prefers large domains of a single monomer. However, the nonlocal term due to molecular connectivity prefers small oscillations between domains of each monomer. The effect of all three is to set a mesoscopic scale for microseparation into metastable states (local minimizers of $E_{\varepsilon, \sigma}$).

Experimentally and numerically, it is well known that in the regimes of interest, the final states prefer periodic structures such as lamellar, spherical, tubular, double-diamond geometries, bicontinuous gyroids (see for example, [4], [3], [13], [11], and [12]). For the case where the length of the A subchains is of the same order as the B (i.e., $m = 0$), a lamellar structure is observed. The natural question arises as to the scale of the optimum period and the extent to which it is determined via minimization of the total free energy. Alternatively, one can approach this fundamental question by asking: In the material parameter regime of interest, how does the minimum energy scale with respect to the material parameters, and which structures attain this optimal scaling? Once a specific ansatz is set for the periodic structure, it is straightforward to optimize within this ansatz and determine the optimal period size ([22], [4]). One can also infer such information via formal dimensional analysis ([3]). These calculations all yield that the domain width (or periodicity) scales like $(\varepsilon/\sigma)^{\frac{1}{3}}$, or in terms of the polymerization index \mathcal{N} , like $\mathcal{N}^{\frac{1}{3}}$. This scaling law has been experimentally confirmed in [10]. While these calculations provide a lot of physical insight, they leave open the fundamental question of what exactly sets the optimal scale. Are periodic structures truly minimizing, or could a nonperiodic geometry yet to be observed and constructed by an ingenious theorist result in even lower energy? As noted by Bates and Fredrickson [4] in *Physics Today*, “A limitation of current theoretical techniques is that they proceed by assuming a periodic structure, computing its free energy and then comparing that free energy to the free energy of other candidate structures. Such calculations run the risk of overlooking complex three-dimensional microphases that have not been previously identified.” In order to address these questions, one needs to examine this variational problem in its full generality from a mathematically more sophisticated point of view, one which in particular allows for a fuller analysis of the competition between the terms in the energy. While these questions have recently been addressed, first in solid-solid phase transitions by Kohn and Müller [16], and then by Choksi, Kohn, and Otto in micromagnetics [5] and superconductivity [6], it was Nishiura and Ohnishi [21] and later, Ohnishi et al. [23] who first addressed them in the present context of diblock copolymers.

To address these issues, Ohnishi et al. [23] considered (\mathcal{P}) in one space dimension. In order to determine the precise energy scaling law, they worked with the extra assumption

that admissible structures were what they called “n-layered” solutions (see [23] for the definition). They concluded that within this smaller class, the global minimizer had a period of order $(\varepsilon/\sigma)^{\frac{1}{3}}$ and an energy of order $\varepsilon^{\frac{2}{3}}\sigma^{\frac{1}{3}}$. That is, they determined the principal part of the asymptotic expansion of both the energy and optimum period. Moreover, they worked with a very general potential W (possibly nonsymmetric) and determined exactly the coefficients of the principal term—in particular, the dependence on m .

The goal here is to obtain a similar result in three dimensions with no a priori assumptions (bias) on admissible geometries. Our result, however, does not give the exact value of the constant, nor the dependence on W . We take the simplest case of a symmetric double-well energy and $m = 0$. We use an interpolation inequality (Lemma 2.1) to give a lower bound on the energy for any admissible u that is valid throughout the parameter regime in question. It is straightforward to show that, within this parameter regime, a simple periodic laminate with optimized period attains this optimal scaling, and thus up to primary order cannot be improved upon. Thus we prove (Theorem 3.2) that in the regime (1.2), the principal part of the asymptotic expansion of $E_{\varepsilon,\sigma}$ is

$$E_{\varepsilon,\sigma} \sim \varepsilon^{\frac{2}{3}}\sigma^{\frac{1}{3}}.$$

With the aid of lower bounds, it is also possible to prove that the $(\varepsilon/\sigma)^{\frac{1}{3}}$ scaling for the domain period size actually holds *on average* for *any* absolute minimizer (see Remark 3.3 for details).

It would also be of interest to determine the optimal scaling with respect to m for the case $m \neq 0$. As one monomer becomes dominant on average, one would expect that isoperimetric factors make energetically preferable spherical or tubular periodic structures; indeed, this is experimentally observed (see [4], [22] and the references therein). The methods of this article could also be applied to the nonsymmetric case to give the optimal scalings in ε and σ . However, the interpolation inequality here is not sensitive enough to capture the optimal scaling with respect to m (see [6]). Moreover, lower and upper bounds do not determine the exact numerical value of the constant for the principal part of the asymptotic expansion for the minimum energy; they only give bounds on its numerical value.

While these lower and upper bounds do provide a first step at an analysis which is devoid of any preassigned bias for the separation geometry, it is important to not overestimate their power in characterizing the ground state configurations. They give the scaling of the ground state energy, providing one with a litmus test to which one can either admit or rule out different patterns. They also give information on the average domain scale of a ground state configuration. However, they do not characterize all configurations in this minimum state, and they say nothing for example, about symmetries, degeneracies, uniqueness. To gain a deeper insight into the energy landscape, analyze further properties of ground state configurations, and also to determine the constant for the principal part of the minimum energy, the natural approach would be to let ε tend to zero and examine the asymptotic limit of the problem.

De Giorgi’s notion of *Gamma convergence* provides an excellent framework for analyzing the asymptotics of the energy functional directly. Current work [1] using the new machinery of Alberti and Müller [2] is based upon fixing a point $s \in \Omega$, a value

for σ , and blowing up a minimizer u_ε of $E_{\varepsilon,\sigma}$ on the scale $(\varepsilon/\sigma)^{\frac{1}{3}}$. Specifically, for a minimizing sequence u_ε , one considers

$$R_s^\varepsilon u(t) := u_\varepsilon \left(s + \frac{\varepsilon^{\frac{1}{3}}}{\sigma^{\frac{1}{3}}} t \right),$$

and examines the asymptotics in ε of this new function of t (the microscopic variable) either directly or via their new concept of a *Young measure on a micropattern*. According to the results of the present paper (Theorem 3.2 and Remark 3.4), this is the correct scale to focus on, and hence the approach of [2] allows one to focus on this scale and eliminate all finer scales. In one space dimension, this new machinery can easily be applied for our problem (\mathcal{P}) to obtain the scaling in m (derived in [23]) and, more importantly, to give rigorous meaning to the statement that any minimizer to (\mathcal{P}) is *locally nearly periodic* with period $(\varepsilon/\sigma)^{\frac{1}{3}}$. Work in higher space dimensions is in progress ([1]), and could shed much more information about minimizing states than just upper and lower bounds. A related approach by Otto for micromagnetics [26] is similar in spirit in that it looks at a renormalization of the total energy where the rescaled limiting behavior of the associated Green's function is analyzed directly. This work could also prove to be a powerful new tool for many nonlocal problems.

We should note that the Gamma limit for the appropriately scaled (\mathcal{P}) has been computed and analyzed within the regime $\varepsilon \sim \sigma \ll 1$ in [28]. A similar result was found independently in [7]. However, it is exactly in this regime that the asymptotics do not involve any interactions between the first two terms of the energy and the third nonlocal term. Specifically, this regime entails considering

$$\frac{E_{\varepsilon,\sigma}(u)}{\varepsilon} := \int_{\Omega} \varepsilon |\nabla u|^2 + \frac{1}{\varepsilon} W(u) + \left| (-\Delta)^{-\frac{1}{2}} (u - m) \right|^2 dx.$$

Since the nonlocal energy is a continuous perturbation of the standard Modica-Mortola energy (the first two terms above), the Gamma limit calculation is essentially of the same difficulty with or without the nonlocal term.

Finally, we must mention the relationship between the functional (1.1) and the functional introduced by Müller in [20]. Consider as we do the case where $m = 0$. As noted by [23], their one-dimensional version of (1.1) bears striking resemblance to Müller's functional:

$$I^\varepsilon(v) = \int_0^1 \varepsilon^2 |v_{xx}|^2 + W(v_x) + v^2 dx. \quad (1.5)$$

Indeed, setting $u = v_x$, one immediately sees the connection, and notes that in one space dimension the nonlocal energy is in fact local: Every function in L^2 is itself a derivative! Of course this is not the case in higher dimensions, but the analogue for higher dimensions of the L^2 norm of the antiderivative is the nonlocal energy, or as seen by (1.4), the H^{-1} norm. Thus, the functional (1.1) can be viewed as Müller's functional in higher space dimensions. From (1.5), one can easily see why the third term prefers fine structure. In fact, if $\varepsilon = 0$, a saw-tooth function $v(x)$ with slopes ± 1 lowers its L^2 norm with more oscillations. Hence the minimum energy is zero but is not attained. If $\varepsilon > 0$, such oscillations are penalized and one expects a fine scale structure. In [23], they noted that

the extension of Müller's functional to a nonsymmetric double well potential presents several difficulties, and their paper, which uses an entirely different machinery, can be viewed as an extension of Müller's result for a nonsymmetric double well potential (with $m \neq 0$).

We remark that in some sense this is the simplest application of interpolation for a rigorous scaling law. Indeed, the functional (1.1) is simpler than other nonlocal energy functionals studied in [5] and [6]; for example, the well-known Landau-Lifshitz-Brown micromagnetics functional ([15]). In [5] and [6], the vector-valued nature of the problems gave rise to an "extra dimension" for the pattern formation. Indeed, periodic structures, like those observed in diblock copolymer melts, were shown to *not* be energy minimizing. Rather, energy minimization dictated a reduction in domain width, so-called branching, in a set direction as one approached the sample boundary, the set direction being the easy magnetization axis for uniaxial ferromagnets and the direction of the applied field for type-I superconductors. Finally, we remark that a functional similar to (1.1) was introduced by Ren and Truskinovsky in [27] to study phase mixtures in a 1-D elastic bar.

2. An Interpolation Inequality

Throughout this paper, we will not be specific about the values of constants (all positive). We will frequently use C to denote a generic positive constant that may change from place to place. We will use numerical indices (e.g., c_1, C_1) for specific constants whose value we wish to keep track of. We make the following assumptions on the double-well potential W . They all hold for the generic examples,

$$W(z) = (1 - z^2)^2 \quad \text{or} \quad W(z) = 1 - z^2,$$

and capture the essential features of these examples. We have not tried to find the most general hypotheses for which our analysis holds.

(H1) $W(z): [-1, 1] \rightarrow \mathbf{R}^+$ is an even C^2 function with zeros only at $z = \pm 1$.

(H2) $W'(z) < 0$ for $z \in (0, 1)$.

(H3) $(\sqrt{W(z)})'' < 0$ for $z \in (-1, 1)$.

We note that these hypotheses imply the following two inequalities hold. There exists a constant $C > 0$ depending only on W , such that for all $z \in [-1, 1]$,

$$z^2 + W(z) > C. \quad (2.1)$$

Let $\phi: [-1, 1] \rightarrow \mathbf{R}$ be the C^1 function such that $\phi(0) = 0$ and $\phi'(z) = \sqrt{W(z)}$. There exists a constant $C > 0$ depending only on W such that for any $z_1, z_2 \in [-1, 1]$,

$$|z_1 - z_2|^2 \leq C|\phi(z_1) - \phi(z_2)|. \quad (2.2)$$

As in *domain theory* for micromagnetics (cf. [15]), a common approach to finding the minimum energy is to a priori assume a rigid one or two dimensional ansatz for the microphase patterns with basically one degree of freedom. One computes the energy of such a structure, and minimization with respect to the free variable leads to the "optimal"

energy and scale. Alternatively we can think of this approach as computing the energy within this ansatz and “renormalizing” in the sense that one factors out of the expression the expected optimal scaling. One then minimizes what remains with respect to the free variable, and finds that in the parameter regime of interest, the minimum is some fundamental constant, i.e., does not depend on the material parameters. The approach of our lower bound is similar in spirit but we make no a priori assumption on what the three-dimensional pattern looks like. After renormalization of the energy computed for any structure, what one is left with is a certain weighted (with respect to the material parameters) sum of three terms which include the H^1 and H^{-1} norms. We prove that this sum is always bounded below by a fundamental constant. This was exactly the approach taken in [5] and [6]. However, there we needed an interpolation inequality between the spaces BV (functions of bounded variation), H^{-1} (or $H^{-\frac{1}{2}}$), and L^2 . A similar inequality holds, where the BV norm is essentially replaced by the sum of the H^1 norm and the double-well energy. The following modifications for the proof of this new inequality were shown to me by F. Otto [25].

Lemma 2.1. *Let $u \in H^1(\Omega)$ with $|u(\mathbf{x})| \leq 1$ for all $\mathbf{x} \in \Omega$. Then there exists a constant c_2 such that for all positive integers N and $\lambda > 0$,*

$$\int_{\Omega} |u|^2 d\mathbf{x} \leq c_2 \left\{ \frac{1}{N} \left(\int_{\Omega} \lambda |\nabla u|^2 + \frac{1}{\lambda} W(u) d\mathbf{x} \right) + \sum_{\mathbf{n} \in \mathbf{Z}^3} \min \left\{ 1, \frac{N^2}{|\mathbf{n}|^2} \right\} |u_{\mathbf{n}}|^2 \right\}. \quad (2.3)$$

Proof. The proof is similar to that of Lemma 2.3 in [5]. There it was presented in two dimensions, but the same proof would work in three dimensions or higher. We will apply the inequality in three dimensions and hence state the proof as such. For completeness, we include the necessary modifications for

$$\lambda \int_{\Omega} |\nabla u|^2 d\mathbf{x} + \frac{1}{\lambda} \int_{\Omega} W(u) d\mathbf{x} \quad \text{replacing} \quad \int_{\Omega} |\nabla u| d\mathbf{x}.$$

Let $\phi: [-1, 1] \rightarrow \mathbf{R}$ be the C^1 function such that $\phi(0) = 0$ and $\phi'(z) = \sqrt{W(z)}$. By the elementary Cauchy inequality,

$$2 \int_{\Omega} |\nabla \phi(u)| d\mathbf{x} \leq \lambda \int_{\Omega} |\nabla u|^2 d\mathbf{x} + \frac{1}{\lambda} \int_{\Omega} W(u) d\mathbf{x}. \quad (2.4)$$

Now fix an integer $N > 0$. We show that the same linear operator $T_N: L^2(\Omega) \rightarrow L^2(\Omega)$ constructed in [5] satisfies

$$\begin{aligned} \int_{\Omega} |u - T_N u|^2 d\mathbf{x} &\leq C_1 \frac{1}{N} \int_{\Omega} |\nabla \phi(u)| d\mathbf{x} \quad \text{and} \\ \int_{\Omega} |T_N u|^2 &\leq C_2 \sum_{\mathbf{n} \in \mathbf{Z}^3} \min \left\{ 1, \frac{N^2}{|\mathbf{n}|^2} \right\} |u_{\mathbf{n}}|^2, \end{aligned} \quad (2.5)$$

for constants C_1, C_2 independent of N . Hence with (2.4), the lower bound (2.3) will follow. The operator T_N is constructed as follows. Fix $\eta \in C_0^\infty(\Omega)$ such that $\int_{\Omega} \eta = 1$.

We define a partition of Ω into N^3 subcubes $\Omega_{\mathbf{m}}$ where $\mathbf{m} \in \{0, \dots, N-1\}^3$, and a rescaled version of η , $\eta_{\mathbf{m}}$ with support in $\Omega_{\mathbf{m}}$, that is,

$$\Omega_{\mathbf{m}} := \frac{1}{N}(\mathbf{m} + \Omega), \quad \frac{1}{N^3}\eta_{\mathbf{m}}\left(\frac{1}{N}(\mathbf{m} + \mathbf{x})\right) = \eta(\mathbf{x}).$$

Finally we define the operator T_N by

$$T_N u := \int_{\Omega_{\mathbf{m}}} u \eta_{\mathbf{m}} d\mathbf{x} \quad \text{on each square } \Omega_{\mathbf{m}}.$$

As in Lemma 2.3 in [5], to prove the first inequality of (2.5), it suffices to prove there exists a constant C such that for all $u \in H^1(\Omega)$,

$$\int_{\Omega} \left| u - \int_{\Omega} u \eta d\mathbf{x} \right|^2 d\mathbf{x} \leq C \int_{\Omega} |\nabla \phi(u)| d\mathbf{x}. \quad (2.6)$$

To see this, note that

$$\int_{\Omega} |u - T_N u|^2 d\mathbf{x} = \sum_{\mathbf{m}} \int_{\Omega_{\mathbf{m}}} \left| u - \int_{\Omega} u \eta_{\mathbf{m}} d\mathbf{x} \right|^2 d\mathbf{x}.$$

Hence it suffices to prove that there exists a constant C such that for all $u \in H^1(\Omega_{\mathbf{m}})$,

$$\int_{\Omega_{\mathbf{m}}} \left| u - \int_{\Omega_{\mathbf{m}}} u \eta_{\mathbf{m}} d\mathbf{x} \right|^2 d\mathbf{x} \leq C_1 \frac{1}{N} \int_{\Omega_{\mathbf{m}}} |\nabla \phi(u)| d\mathbf{x}, \quad (2.7)$$

and then sum over all \mathbf{m} . Inequality (2.7) follows from (2.6) by a simple rescaling argument. We must prove (2.6). To this end,

$$\begin{aligned} \int_{\Omega} \left| u(\mathbf{x}) - \int_{\Omega} u(\mathbf{y}) \eta(\mathbf{y}) d\mathbf{y} \right|^2 d\mathbf{x} &\leq \int_{\Omega} \int_{\Omega} |u(\mathbf{x}) - u(\mathbf{y})|^2 d\mathbf{x} d\mathbf{y} \\ &\leq C \int_{\Omega} \int_{\Omega} |\phi(u(\mathbf{x})) - \phi(u(\mathbf{y}))| d\mathbf{x} d\mathbf{y}. \end{aligned}$$

Here we made use of Jensen's inequality in the first inequality and (2.2) in the second. Thus it remains to show for $\psi = \phi \circ u$,

$$\int_{\Omega} \int_{\Omega} |\psi(\mathbf{x}) - \psi(\mathbf{y})| d\mathbf{x} d\mathbf{y} \leq C \int_{\Omega} |\nabla \psi(\mathbf{x})| d\mathbf{x}.$$

This follows from the convexity and boundedness of Ω . To see this, note that

$$|\psi(\mathbf{x}) - \psi(\mathbf{y})| = \left| \int_0^1 \nabla \psi(t\mathbf{x} + (1-t)\mathbf{y}) \cdot (\mathbf{x} - \mathbf{y}) dt \right| \leq C \int_0^1 |\nabla \psi(t\mathbf{x} + (1-t)\mathbf{y})| dt.$$

Hence,

$$\begin{aligned} \int_{\Omega} \int_{\Omega} |\psi(\mathbf{x}) - \psi(\mathbf{y})| d\mathbf{x} d\mathbf{y} &\leq C \int_0^{\frac{1}{2}} \int_{\Omega} \int_{\Omega} |\nabla \psi(t\mathbf{x} + (1-t)\mathbf{y})| d\mathbf{y} d\mathbf{x} dt \\ &\quad + C \int_{\frac{1}{2}}^1 \int_{\Omega} \int_{\Omega} |\nabla \psi(t\mathbf{x} + (1-t)\mathbf{y})| d\mathbf{x} d\mathbf{y} dt. \end{aligned}$$

Changing variables from \mathbf{y} to \mathbf{z} in the inner integral of the first term on the right, and \mathbf{x} to \mathbf{z} in the inner integral of the second term where $\mathbf{z} = t\mathbf{x} + (1-t)\mathbf{y}$, and noting that for fixed \mathbf{x} or \mathbf{y} in Ω , the respective sets $\{t\mathbf{x} + (1-t)\Omega\}$ or $\{t\Omega + (1-t)\mathbf{y}\}$ are both contained in Ω (by convexity of Ω), we have

$$\begin{aligned} \int_{\Omega} \int_{\Omega} |\psi(\mathbf{x}) - \psi(\mathbf{y})| d\mathbf{x} d\mathbf{y} &\leq C \int_0^{\frac{1}{2}} \int_{\Omega} \frac{1}{(1-t)^3} \int_{\Omega} |\nabla\psi(\mathbf{z})| d\mathbf{z} d\mathbf{x} dt \\ &\quad + C \int_{\frac{1}{2}}^1 \int_{\Omega} \frac{1}{t^3} \int_{\Omega} |\nabla\psi(\mathbf{z})| d\mathbf{z} d\mathbf{y} dt, \end{aligned}$$

and the first inequality of (2.5) follows. The proof of the second inequality of (2.5) follows verbatim from Lemma 2.3 of [5] with the obvious dimensional changes appropriate to $\Omega \in \mathbf{R}^3$. \square

3. A Scaling Law in Three Dimensions

A simple application of Lemma 2.1 gives a rigorous lower bound for the total free energy of *any* admissible structure. The constants in the following hypothesis $0 < \varepsilon < 2\sigma < \frac{1}{3}$ are simply for convenience in proving the lower and upper bounds.

Theorem 3.1. *There exists a constant c_1 which depends only on the structure of the double-well energy W , such that if $0 < \varepsilon < 2\sigma < \frac{1}{3}$,*

$$\min_{u \in \mathcal{A}} E_{\varepsilon, \sigma} \geq c_1 \varepsilon^{\frac{2}{3}} \sigma^{\frac{1}{3}}.$$

Proof. Let $u \in \mathcal{A}$. By (1.4),

$$\begin{aligned} \frac{E_{\varepsilon, \sigma}(u)}{\sigma} &= \int_{\Omega} \frac{\varepsilon^2}{\sigma} |\nabla u|^2 + \frac{1}{\sigma} W(u) + \sum_{\mathbf{n} \in \mathbf{Z}^3} \frac{|u_{\mathbf{n}}|^2}{|\mathbf{n}|^2} \\ &= \frac{\varepsilon^{\frac{2}{3}}}{\sigma^{\frac{2}{3}}} \left[\frac{\varepsilon^{\frac{1}{3}}}{\sigma^{\frac{1}{3}}} \int_{\Omega} \left(\varepsilon |\nabla u|^2 + \frac{2W(u)}{3\varepsilon} \right) d\mathbf{x} \right. \\ &\quad \left. + \frac{\sigma^{\frac{2}{3}}}{\varepsilon^{\frac{2}{3}}} \sum_{\mathbf{n} \in \mathbf{Z}^3} \frac{|u_{\mathbf{n}}|^2}{|\mathbf{n}|^2} \right] + \frac{1}{3\sigma} \int_{\Omega} W(u) d\mathbf{x} \\ &\geq \frac{\varepsilon^{\frac{2}{3}}}{\sigma^{\frac{2}{3}}} \left[\frac{\varepsilon^{\frac{1}{3}}}{\sigma^{\frac{1}{3}}} \int_{\Omega} \left(\varepsilon |\nabla u|^2 + \frac{2W(u)}{3\varepsilon} \right) d\mathbf{x} \right. \\ &\quad \left. + \sum_{\mathbf{n} \in \mathbf{Z}^3} \min \left\{ 1, \frac{\sigma^{\frac{2}{3}}}{\varepsilon^{\frac{2}{3}} |\mathbf{n}|^2} \right\} |u_{\mathbf{n}}|^2 \right] + \frac{1}{3\sigma} \int_{\Omega} W(u) d\mathbf{x}. \end{aligned}$$

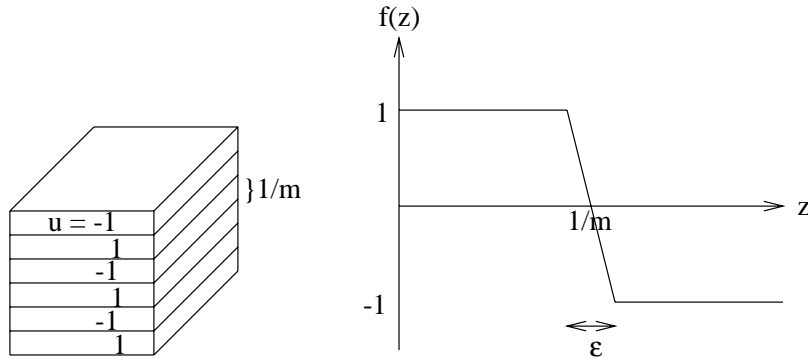


Fig. 2. (left) Periodic laminate structure which up to primary order is minimizing; (right) u_b at the interfaces.

Now we are in a position to apply Lemma 2.1 to the squared brackets with $\lambda = \varepsilon$ and $N \sim \sigma^{\frac{1}{3}} \varepsilon^{-\frac{1}{3}}$ which by hypothesis is possible:

$$\begin{aligned} \frac{E_{\varepsilon, \sigma}(u)}{\sigma} &\geq C \frac{\varepsilon^{\frac{2}{3}}}{\sigma^{\frac{2}{3}}} \left(\int_{\Omega} u^2 d\mathbf{x} \right) + \frac{1}{3\sigma} \int_{\Omega} W(u) d\mathbf{x} \\ &\geq C \frac{\varepsilon^{\frac{2}{3}}}{\sigma^{\frac{2}{3}}} \left(\int_{\Omega} u^2 + W(u) d\mathbf{x} \right) \\ &\geq C \frac{\varepsilon^{\frac{2}{3}}}{\sigma^{\frac{2}{3}}}, \end{aligned}$$

where in the second line, we use that by hypothesis,

$$\frac{\varepsilon^{\frac{2}{3}}}{\sigma^{\frac{2}{3}}} < \frac{1}{3\sigma},$$

and in the third line, inequality (2.1). Thus for some constant c_1 which depends only on the structure of W , we have

$$E_{\varepsilon, \sigma}(u) \geq c_1 \varepsilon^{\frac{2}{3}} \sigma^{\frac{1}{3}},$$

and the result follows. \square

As for the upper bound, it is straightforward to check that a simple lamellar structure with optimal period achieves the scaling of Theorem 3.1. Let $u_b(x, y, z) := f(z)$ where the structure of f can be easily inferred from Figure 2: the right-hand side of Figure 2 graphs f over the first period, i.e., for $z \in [0, \frac{2}{m} - \frac{\varepsilon}{2}]$. We choose an even integer m such that

$$\frac{1}{m} \sim \frac{\varepsilon^{\frac{1}{3}}}{\sigma^{\frac{1}{3}}}, \quad (3.1)$$

i.e., choose the closest even integer to $\sigma^{\frac{1}{3}} \varepsilon^{-\frac{1}{3}}$ (note that by hypothesis, $\sigma^{\frac{1}{3}} \varepsilon^{-\frac{1}{3}} > 2$). The interfacial energy is easily found to be of order $\varepsilon^{\frac{2}{3}} \sigma^{\frac{1}{3}}$. For the double-well energy, one

easily sees, using a crude bound like $W(\cdot) \leq W(0)$, that this term contributes an energy below $C\varepsilon^{\frac{2}{3}}\sigma^{\frac{1}{3}}$. Turning to the nonlocal energy, a simple scaling argument implies that the nonlocal energy of u_b , written in terms of the Fourier coefficients (cf. (1.4)), scales like $\sigma/m^2 \sim \varepsilon^{\frac{2}{3}}\sigma^{\frac{1}{3}}$. Thus for some fundamental constant C ,

$$E_{\varepsilon,\sigma}(u_b) \leq C\varepsilon^{\frac{2}{3}}\sigma^{\frac{1}{3}}.$$

Note that if one had kept the number of oscillations m as a variable throughout these calculations and finally optimized with respect to m , one would have come up with (3.1). We have proved:

Theorem 3.2. *There exist constants c_1, C_1 depending only on the structure of W such that if $0 < \varepsilon < 2\sigma < \frac{1}{3}$,*

$$c_1\varepsilon^{\frac{2}{3}}\sigma^{\frac{1}{3}} \leq \min_{u \in \mathcal{A}} E_{\varepsilon,\sigma} \leq C_1\varepsilon^{\frac{2}{3}}\sigma^{\frac{1}{3}}.$$

Remark 3.3. The global minimizer to (P) does exist (a simple application of the direct method of the calculus of variations). Following [5], one could further obtain a result pertaining to the average length scale of all global minimizers. Based upon the ansatz of phase separation, we would replace (P) with

$$\min_{u \in \mathcal{S}} E_{\varepsilon,\sigma}^{sharp} = \int_{\Omega} \varepsilon |\nabla u| + \sigma \sum_{\mathbf{n} \in \mathbb{Z}^3} \frac{|u_{\mathbf{n}}|^2}{|\mathbf{n}|^2},$$

where

$$\mathcal{S} := \left\{ u \in BV(\Omega, \{1, -1\}) \mid \int_{\Omega} u \, d\mathbf{x} = 0 \right\}.$$

$BV(\Omega, \{1, -1\})$ is the space of functions of bounded variation taking on the values 1 or -1 , and the first term in the energy represents the total variation of the distributional derivative which, in this case, is simply twice the total area of the interfaces. Using the sharp interface interpolation inequality, i.e., Lemma 2.1 of [5], it is possible to show that for any pattern satisfying the optimal energy scaling law, the lower bound holds separately for both the surface energy and the nonlocal energy in $E_{\varepsilon,\sigma}^{sharp}$. With this in hand, one proves the following: Let u^* be a minimizer (which also exists) of $E_{\varepsilon,\sigma}^{sharp}$, and let

$$d^* := \left(\int_{\Omega} |\nabla u^*| \right)^{-1}.$$

Since $|\Omega| = 1$, d^* represents the average domain width (or average period) across the sample. Then $d^* \sim (\varepsilon/\sigma)^{\frac{1}{3}}$, i.e., there exist fundamental constants c_3, C_3 such that if $0 < \varepsilon < 2\sigma < \frac{1}{3}$,

$$c_3 \frac{\varepsilon^{\frac{1}{3}}}{\sigma^{\frac{1}{3}}} \leq d^* < C_3 \frac{\varepsilon^{\frac{1}{3}}}{\sigma^{\frac{1}{3}}}.$$

Remark 3.4. The analysis of this paper is based upon the particular form of the kernel (Greens function) in (1.3). A similar analysis with a different interpolation inequality could be applied for the L^2 norm squared of any negative power of $(-\Delta)$, i.e., any negative Sobolov norm. Of course the resulting scaling law would depend on this power. One would suspect that the same scaling law should hold for a kernel that differed from our Greens function only at its tail end: for example, with an exponentially decaying tail. However, the methods of this paper would not directly apply to this modified kernel.

This alerts us as to two important directions for future research. First, one would like to characterize the class of kernels whose inclusion would result in the same scaling behavior for minimizers and perhaps even the same morphology for self-assembly patterns; their predictions agree with the clear experimental phase diagram for the different self-assemblies; see for example [4]. The previously mentioned method of Alberti and Müller ([2]) could prove very useful here. Second, one should revisit the derivation of (1.1) in [22], and moreover go back to older and newer models proposed by Leibler [17], Helfand [14], and Matsen and Schick [18] to see what exactly determines the behavior of the kernel, and which kernels should, at least from the point of the statistical physics, give rise to an equivalent functional, one with similar topologies and scales for its ground states. In doing so, it would be instructive to write the free energy functional not in terms of ε (as is the norm for applied mathematicians), σ , and m but rather in terms of the standard material parameters in the vast copolymer literature: the Flory-Huggins interaction parameter χ , the index of polymerization \mathcal{N} , and the molecular weight ratio f (essentially our m). Indeed, for the purposes of the phase diagram, it is really f and the product $\chi\mathcal{N}$ which are relevant (cf. [4]).

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