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Mathematical Aspects of Microphase Separation of Diblock Copolymers

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Abstract

Diblock copolymer melts, dubbed "designer materials", have the remarkable ability to self-assemble into various ordered structures. These structures are key to the many properties that make diblock copolymers of great technological interest. The density functional theory of Ohta and Kawasaki leads to a nonlocal variational problem, and presents an excellent setting for the analysis of microphases.

In this note we will first discuss the origins and derivation of this theory, presenting it in connection with the self-consistent mean field theory. Then, focusing on what is know as the strong segregation regime, we will discuss some analytical techniques which provide insight on the scales of minimizing structures (phases). These techniques have the advantage that they are ansatz-free, that is they are not based upon any preassigned bias for the phase geometry. In particular, we will derive a scaling law for the minimum energy in three space dimensions, and will address properties of optimal structures achieving this scaling law.

This note includes joint work with X. Ren (Utah State University) and work in progress with G. Alberti (University of Pisa) and F. Otto (University of Bonn).

1 The Physical Problem

A diblock copolymer is a linear-chain molecule consisting of two subchains joined covalently to each other. One of the subchains is made of monomers of type A and the other of type B. Below a critical temperature, even a weak repulsion between unlike monomers A and B induces a strong repulsion between the subchains, causing the subchains to segregate. A macroscopic segregation whereby the subchains detach from one another can not occur because the chains are chemically bonded. Rather, in a system of many such macromolecules, the immisibility of these monomers drives the system to form structures which minimize contacts between the unlike monomers and this tendency to separate the monomers into A and B-rich domains is counter balanced by the entropy cost associated with chain stretching. Because of this energetic competition, a phase separation on a mesoscopic scale with A and B-rich domains emerges. The mesoscopic domains which are observed are highly regular periodic structures; for example lamellar, bcc centered spheres, circular tubes, and bicontinuous gyroids (see for example, [4], [11]). These ordered structures are key to the material properties which make diblock copolymers of great technological importance.

Three dimensionless material parameters are needed for modeling the microphase separation: χ, the Flory-Huggins interaction parameter measuring the incompatibility of the two monomers and is inversely proportional to the temperature; N, the index of polymerization measuring the number of monomers per macromolecule; and a, the relative length of the A-monomer chain compared with the length of the whole macromolecule. In the mean field approximation, where thermal fluctuations are ignored, one finds that the microphase separation depends only on the two quantities χN and a. The phase diagram (either theoretically or experimentally constructed) indicates several regimes for the phase separation. In particular, for a fixed value of a one finds with increasing χN; a disordered regime wherein the melt exhibits no observable phase separation, the *weak segregation regime* (WSR) where the size of the A and B-rich domains are of roughly of

the same order as the interfacial (overlapping) regions around the bonding points, an *intermediate segregation regime*, and the *strong segregation regime* (SSR) wherein the domain size is much larger than the interfacial length. In the SSR, it has been observed (*cf.* [12, 13]) that the domain size scales like $\chi^{1/6} N^{2/3}$ where as the interfacial length scales like $\chi^{-1/2}$.

2 Ohta-Kawasaki Density Functional Theory

In [22], Ohta and Kawasaki derived a density functional theory[1] (DFT) which reduces to the minimization of a *Cahn-Hilliard-like* free energy. Following [21, 8], we write the functional in a rescaled, nondimensional form as a function of the relative (averaged) macroscopic monomer density u (i.e. the difference between the averaged A and B monomer densities):

$$E_{\epsilon,\sigma}(u) := \frac{\epsilon^2}{2}\int_D |\nabla u|^2\,d\mathbf{x} + \int_D W(u)\,d\mathbf{x} + \frac{\sigma}{2}\int_D \left|(-\Delta)^{-\frac{1}{2}}(u(x)-m)\right|^2 d\mathbf{x}, \tag{2.1}$$

where Δ is the Laplacian operator with Neumann boundary conditions; D is a subset of R^3 with unit volume (representing the rescaled physical space Ω upon which the melt exists); W has a double-well structure preferring pure A and B phases ($u = \pm 1$); ϵ represents the interfacial thickness (suitably rescaled) at the A and B monomer intersections; and σ is inversely proportional to N^2. More precisely, the parameters ϵ, σ are related to the parameters χ, N, a, $|\Omega|$ via (*cf.* [8])

$$\epsilon^2 = \frac{l^2}{3\,a\,(1-a)\,\chi\,|\Omega|^{2/3}} \qquad \sigma = \frac{36\,|\Omega|^{2/3}}{a^2(1-a)^2\,l^2\,\chi\,N^2}, \tag{2.2}$$

where l denotes the Kuhn statistical length which measures the average distance between two adjacent monomers. Conservation of the order parameter u requires we maintain the constraint

$$\int_D u\,d\mathbf{x} = m = 2a - 1.$$

From this functional it is easy to see the incentive for pattern formation. The double-well term prefers pure phases of A or B monomers, but for $m \neq \pm 1$, the conservation constraint dictates a mixture. Transitions between phases are penalized by the gradient term but the nonlocal term prefers oscillations between phases. The latter is best seen in one space dimension. Indeed, this functional can be regarded as a higher-dimensional analogue of a functional introduced by Müller in [20] as a toy problem for capturing multiple-scales. Let $m = 0$, $\sigma/2 = 1$. Setting $u = v_x$, gives

$$\int_0^1 \frac{\epsilon^2}{2}|v_{xx}|^2 + W(v_x) + v^2\,dx. \tag{2.3}$$

In particular, in one space dimension the nonlocal energy is in fact local: every function in L^2 is itself a derivative. In higher dimensions the analogue for the L^2 norm of the primitive is the nonlocal term in (2.1), which for periodic functions u on the cube is simply the H^{-1} norm squared. From (2.3), one can easily see why the third term induces fine structure. If $\epsilon = 0$ a saw-tooth function $v(x)$ with slopes ± 1 lowers its L^2 norm with increasing oscillations. Hence the minimum energy is zero but is not attained. If $\epsilon > 0$, such oscillations are penalized and one expects the competition to result in oscillations on a fine but specific scale.

3 Derivation of the Ohta-Kawasaki DFT

In this section we give a summary of the main steps in deriving the free energy (2.1). The purpose is to give the reader some idea of how one derives such a functional from the statistical physics of Gaussian chains.

[1] see related work in [3], [16], [20]

We follow [8] but provide few details. The derivation is based on two steps. The first is what is commonly referred to as the Self-Consistent Mean Field Theory (SCMFT) which has been developed and applied over the years by many researchers, see for example [11], [17] and the references therein. The copolymer melt is modeled with a phase space of n of continuous chains which prefer to be *randomly coiled.* Thus we consider a phase space

$$\Gamma = \{r = (r_1, ..., r_n) : r_i \in C([0, N], \mathbf{R}^3)\}$$

equipped with a product measure $d\mu$ consisting essentially of n copies of Wiener measure. The A (B respectively) monomers "occupy" the interval $\mathcal{I}_A = (0, N_A)$ ($\mathcal{I}_B = (N_A, N)$ respectively). Within this space one introduces a monomer interaction Hamiltonian to reflect the immisibility of the different monomer types. At this point one can write the associated partition function Z, the free energy $-\beta^{-1} \log Z$, and Gibbs canonical distribution $D(r)$. Defining the microscopic densities as

$$\rho_k(x, r) = \sum_{i=1}^{n} \int_{\mathcal{I}_k} \delta(x - r_i(\tau))\, d\tau, \;\; k = A, B,$$

the desired macroscopic monomer densities should be given by

$$\langle \rho_k(x) \rangle = \int_\Gamma \rho_k(x, r) D(r)\, d\mu. \;\; k = A, B \tag{3.4}$$

None of these can actually be calculated because of the nonlocal character of the Hamiltonian. The Self-Consistent Mean Field Theory is based upon a variational principle whereby the true free energy is approximated by a minimization over a class of distributions generated by a single external field $U = (U^A, U^B)$ acting separately on the A and B monomers. More specifically, setting

$$H_U(r) = \sum_{i=1}^{n} \sum_{k} \int_{\mathcal{I}_k} U^k(r_i(\tau))\, d\tau.$$

with the resulting partition function and Gibbs canonical distribution

$$Z_U = \int_\Gamma \exp(-\beta H_U(r))\, d\mu, \quad D_U(r) = \frac{1}{Z_U} \exp(-\beta H_U(r)),$$

one approximates the true free energy by minimizing

$$F(U) = \int_\Omega \left[\frac{V^{km}}{2\rho_0} \langle \rho_k(x) \rangle_U \langle \rho_m(x) \rangle_U - U^k(x) \langle \rho_k(x) \rangle_U \right] d\mathbf{x} - \frac{1}{\beta} \log Z_U. \tag{3.5}$$

over all external fields $U = (U^A, U^B)$. Here, $\langle \cdot \rangle_U$ denotes the expectation with respect to $D_U(r)\, d\mu$; β is the reciprocal of the absolute temperature measured in units of (energy)$^{-1}$ (the Boltzmann constant has been set to one); V^{km} represents the interaction parameters with

$$\chi = \beta V^{AB} - (\beta/2)(V^{AA} + V^{BB}) > 0;$$

and $\rho_0 = nN/|\Omega|$ (the average monomer density number). The explicit nature of the external field allows one to compute all the variational integrals via Feynman-Kac integration theory.

The second step entails writing the free energy entirely in terms of the macroscopic monomer density. The first term (i.e. the interaction term) in (3.5) is already written in terms of the monomer density and naturally gives rise to the double-well energy in (2.1). The main step in turning the second and third term in (3.5) to a functional of $\langle \rho \rangle$ involves the inversion of the relationship between the dependence of $\langle \rho \rangle_U$ on βU via the linearization about $\beta = 0$ (i.e. at infinite temperature). This is done via the solutions to the backward and forward modified heat equations which come from the Feynman-Kac integration theory. The details are too cumbersome to summarize here but very briefly, this linearization entails convolution of βU with a certain tensor whose Fourier transform can be computed explicitly. We keep only the short and long range expansions. After some calculations and the introduction of the monomer difference order parameter, we arrive at both the squared gradient and nonlocal term in (2.1), with the respective coefficients reflecting

4 Scaling Laws

Accepting the free energy (2.1), the natural question arises as to what minimizers look like for small ϵ; or worded slightly differently, what are necessary properties for configurations to be minimizing. One approach could be via the associated gradient flow dynamic equations which for the conserved order parameter u would be the *Cahn-Hilliard dynamics*, formally written as

$$u_t = \triangle \frac{\delta F}{\delta u}.$$

More precisely, this is gradient flow with respect to the H^{-1} norm (see [10]). Here we take a different approach, namely a *direct method*, and address the issue of scaling of the minimum energy and the resulting consequences on minimizing structures. That is, we ask: 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?

The simplest approach to this question is based upon setting an ansatz for possible structures with a few degrees of freedom, and then minimizing the free energy amongst these structures alone. This approach, often dubbed *domain theory* is ubiquitous; for example Landau used it in his study of ferromagnetism and type-I superconductivity (*cf.* [15]). In the present context of copolymers, this has been done to to determine the optimal period size ([22], [4]) which one can also infer via formal dimensional analysis ([3]). These calculations all yield that the domain width (or periodicity) scales like $(\epsilon/\sigma)^{1/3}$, or in terms of N, like $N^{2/3}$. This scaling law has been experimentally confirmed in [12, 13]. 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?

To address these questions rigorously, Ohnishi et al [23] worked in one space dimension with the extra assumption that admissible structures were what they called "n-layered" solutions (see [23] for the definition). They concluded[2] that within this smaller class, the global minimizer had a period of order $(\epsilon/\sigma)^{1/3}$, and an energy of order $\epsilon^{2/3}\sigma^{1/3}$. Ren and Wei ([24]) recently obtained the same result with no assumption on admissible structures. In higher space dimensions it is unlikely that minimizing structures are exactly periodic. What then can one prove? One approach, first used in solid-solid phase transformations (*cf.* [14]), is via a geometry-independent lower bound on the total free energy. To motivate this, let us go back to an ansatz driven calculation[3]. We consider an ansatz of lamellar structures with the periodicity d as the only degree of freedom. One can then write the free energy entirely in terms of the material parameters and d: $E_{\epsilon,\sigma}(d)$. Factoring out (*renormalizing*) the conjectured scaling gives

$$E_{\epsilon,\sigma}(d) = \epsilon^{\frac{2}{3}}\sigma^{\frac{1}{3}} F(d,\epsilon,\sigma).$$

One then optimizes in d to find that, in the parameter regime of interest ($0 < \epsilon \leq \sigma < C$),

$$d_{\text{optimal}} \sim (\epsilon/\sigma)^{\frac{1}{3}} \qquad \text{and} \qquad F(d_{\text{optimal}},\epsilon,\sigma) \sim 1. \tag{4.6}$$

For the lower bound, we make no assumption on the domain structure (essentially $u \in H^1$) and after renormalization

$$E_{\epsilon,\sigma}(u) = \epsilon^{\frac{2}{3}}\sigma^{\frac{1}{3}} F(u,\epsilon,\sigma), \tag{4.7}$$

we find that, in the relevant parameter regime,

$$F(u,\epsilon,\sigma) \geq C, \tag{4.8}$$

for some constant C independent of ϵ, σ, and u.

[2]They also deduced the dependence on m $(= 2a - 1)$. Through out this note, we will fix $m \in (-1, 1)$ and do not address scaling issues pertinent to this parameter.

[3]For a detailed look at more complicated ansatz driven calculations see [7]

To be more specific, we follow [5]. Let D be the unit cube, and since we are interested here in the scaling with respect to ϵ and σ, let $m = 0$, and $W(u) = 1 - u^2$. Our approach would give the same scaling in ϵ and σ for $m \in (-1, 1)$ fixed. We work for convenience within the class of admissible states which satisfy the zero flux (Neumann) boundary condition. That is, the class of admissible states $\mathcal{A}$ is,

$$\mathcal{A} := \left\{ u \in H^1(D) \,\middle|\, \frac{\partial u}{\partial \nu}|_{\partial D} = 0, \int_D u \, d\mathbf{x} = 0 \right\},$$

where ν denotes the outer normal to ∂D. Hence,

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

where $u_\mathbf{n}$ ($\mathbf{n} \in \mathbf{Z}^3, \mathbf{n} \neq \mathbf{0}$) are the appropriate Fourier coefficients. This is the H^{-1} norm squared on the space of L^2 functions with zero average. Within this formulation, steps (4.7) and (4.8) require us to bound below the sum

$$\frac{1}{M(\epsilon,\sigma)} \left(\int_\Omega \epsilon |\nabla u|^2 + \frac{1}{\epsilon}(1 - u^2) \, d\mathbf{x} \right) + M^2(\epsilon,\sigma) \sum_{\mathbf{n} \in \mathbf{Z}^3} \frac{|u_\mathbf{n}|^2}{|\mathbf{n}|^2}, \tag{4.9}$$

where in the relevant parameter regime we have $M(\epsilon, \sigma) \geq C$, for some constant $C > 0$. As is well-known from the work of Modica and Mortola (*cf.* [18]), the sum in the parentheses is bounded below by a BV norm of u, and hence we seek an interpolation-like inequality between the spaces BV and H^{-1}. Lemma 2.1 in [5] (following work in [6]) bounds below the sum in (4.9) by the L^2 norm squared of u, and allows us to conclude the desired lower bound (4.8). The upper bound is obtained by following (4.6). We arrive at:

Theorem 4.1 *If* $0 < \epsilon \lesssim \sigma \lesssim 1$[4],

$$\epsilon^{\frac{2}{3}} \sigma^{\frac{1}{3}} \lesssim \min_{u \in \mathcal{A}} E_{\epsilon,\sigma} \lesssim \epsilon^{\frac{2}{3}} \sigma^{\frac{1}{3}}.$$

Here we have adopted the notation that for functions f and g of the parameters ϵ and σ, $f \lesssim g$ means for some constant $C > 0$ independent of ϵ and σ we have $f < C\, g$. In the present context, the constant may in general depend on the structure of W and m.

While the approach of matching upper and lower energy bounds may not appear to say anything about the minimizer's domain size in the way the ansatz driven calculation (4.6) did, it does yield ansatz-free matching upper and lower bounds for the minimizer's *average* length scale - more precisely for the total interfacial perimeter per unit volume (see [5, 6, 7]). However, we emphasize that Theorem 4.1 does not imply that (for small ϵ) minimizers are periodic structures on the scale $(\epsilon/\sigma)^{1/3}$. It is suggestive that they possess an inherent scale of $(\epsilon/\sigma)^{1/3}$ but certainly one would like a stronger result. In the next section, we present such a result.

5 Uniform distribution of energy in a sharp-interface limit

Here we report on some work in progress with Alberti and Otto ([1]). We are interested in obtaining further rigorous support for the following conjecture: *For ϵ small, minimizers of* (2.1) *are nearly periodic structures on the scale* $(\epsilon/\sigma)^{1/3}$ (*i.e.* $N^{2/3}$). Exactly what one means by *nearly periodic* has of course to be made clear.

One approach is via a sharp-interface limit whereby ϵ tends to zero. We pause to note that one can easily obtain a sharp-interface limiting energy functional by considering (2.1) in terms of the original material parameters (2.2); fixing χ; taking $|\Omega|^{1/3} \sim N^{2/3} l$; and letting N tend to infinity: Thus we keep the sample size of the melt on the same (conjectured) length scale of the domains. One can easily show (*cf.* [8, 25]) that

[4] In [5] this notation was not used but instead particular constants were chosen in the hypothesis $0 < \epsilon \lesssim \sigma \lesssim 1$ for convenience in proving the upper and lower bounds. This is insignificant as it only effects the constants in the conclusion; however, we remark that they were in fact incorrectly chosen for their purpose!

as $N \to \infty$, the functional (2.1) (suitably rescaled) Γ-converges (in the sense of De Giorgi (*cf.* [9, 18])) to a nongenerate sharp-interface variational problem.

In this section, we follow the idea presented in [2] which will in the end result in studying (essentially) the same sharp-interface variational problem. Consider a sequence $u_\epsilon(x)$ ($\epsilon \to 0$) of minimizers of $E_{\epsilon,\sigma}$ and fix a position s in the melt (we will take $s = 0$ for simplicity). We blow up at $s = 0$, sending the scale $(\epsilon/\sigma)^{1/3}$ to 1 and removing all finer scales: That is, consider the functions of a microscopic variable $\mathbf{t}$:

$$v_\epsilon(\mathbf{t}) := u_\epsilon\left(\left(\frac{\epsilon}{\sigma}\right)^{\frac{1}{3}} \mathbf{t}\right).$$

In terms of the blow-ups v_ϵ, the previous conjecture can be rephrased as follows: *v_ϵ tends to periodic functions with period $O(1)$ taking on only the two values ± 1 (corresponding to the pure A and B phases).*

We very briefly present a partial result in support of this conjecture. Our approach is via the asymptotics of the energy written in terms of $v_\epsilon(\mathbf{t})$; thereby capturing the asymptotics of the minimizers themselves. The energy functional on $v_\epsilon(\mathbf{t})$ is defined over domains whose size becomes infinite. Thus we are forced to deal with several issues. The first being that we should naturally be concerned with an appropriate notion of a *spatially local minimizer* (see below). The second pertains to the nonlocal term defined over domains of increasing size (i.e. boundary conditions, the conservation constraint, notion of a local minimizer, etc.). These issues are dealt with by considering a natural *relaxation* of the nonlocal term. Here we will only be concerned with the limiting sharp-interface problem, and hence let us describe this *relaxation* in that context. Let A be a bounded, open set. For $v \in BV(A, \pm 1)$ we introduce a second dependent variable $\mathbf{b}$ coupled to v by the constraint $\operatorname{div} \mathbf{b} = v$ (interpreted in the sense of distributions), and replace the H^{-1} norm squared of v by

$$\min_{\substack{\mathbf{b} \in L^2 \\ \operatorname{div} \mathbf{b} = v}} \int_A |\mathbf{b}|^2.$$

One can then reduce the original variational problem (at least formally[5]) to the following sharp-interface problem:

$$\min \; E(v, \mathbf{b}, A) := \int_A |\nabla v| + |\mathbf{b}|^2 \qquad \text{over} \qquad \operatorname{div} \mathbf{b} = v, \quad v \in BV(A, \pm 1).$$

Now we say $(\tilde{v}, \tilde{\mathbf{b}})$ with $\operatorname{div} \tilde{\mathbf{b}} = \tilde{v}$ is a local minimizer of E on Ω if for all open $A \subset\subset \Omega$ and $(v, \mathbf{b})$, $\operatorname{div} \mathbf{b} = v$, such that $\operatorname{support}(\tilde{\mathbf{b}} - \mathbf{b}) \subset\subset A$, we have $E(\tilde{v}, \tilde{\mathbf{b}}, A) \leq E(v, \mathbf{b}, A)$. Within this framework one can prove an uniform distribution of energy for local minimizers of E. That is, if $(\tilde{v}, \tilde{\mathbf{b}})$ is a local minimizer of E on Ω, then for every $r \geq 1$ and $B(r) \subset \Omega$, we have

$$E(\tilde{v}, \tilde{\mathbf{b}}, B(r)) \sim |B(r)|,$$

where $B(r)$ is a ball of radius r and $\sim$ indicates both $\lesssim$ and $\gtrsim$ with the respective constants independent of $\tilde{v}, \tilde{\mathbf{b}}$, and r. The lower bound for this assertion follows from an interpolation-like argument similar to one used in the previous section. The upper bound follows from direct construction of suitable comparison fields. The details will be presented in [1].

6 Remarks

We have discussed issues and results pertaining to scales and the distribution of energy for minimizers of the Ohta-Kawasaki energy in the SSR. Whereas these results seem encouraging in terms of building ansatz-free tools for capturing properties of the microphases, one should be alerted to the fact that the derivation of this functional was based upon the linearization about $\beta = 0$ (i.e. about infinite temperature). Thus the

[5]The connection via Γ-convergence is still formal as we do not as yet have a compactness result at the ϵ-level (*cf.* [9]) for this type of local minimizers.

physical validity of the density functional theory in regimes other than the WSR remains unclear. In the SSR, it does seem to predict the basic scaling features of the domain size; however, one must be skeptical as to whether or not it retains all the essential physics of the problem - as the pure SCMFT seems to [4, 17]. On the other hand, some recent simulations of the bicontinuous gyroid phase of Teramoto and Nishiura ([26]) indicate that this theory does predict rather nonstandard structures (i.e. other than lamellar, cylindrical and spherical) which have been observed at temperatures placing one in the intermediate segregation regime, and have been previously predicted by the SCMFT ([17]).

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