

On the Derivation of a Density Functional Theory for Microphase Separation of Diblock Copolymers

Rustum Choksi¹ and Xiaofeng Ren²

Received September 24, 2002; accepted April 14, 2003

We consider here the problem of phase separation in copolymer melts. The Ohta–Kawasaki density functional theory gives rise to a nonlocal *Cahn–Hilliard-like* functional, promoting the use of ansatz-free mathematical tools for the investigation of minimizers. In this article we re-derive this functional as an offspring of the self-consistent mean field theory, connecting all parameters to the fundamental material parameters and clearly identifying all the approximations used. As a simple example of an ansatz-free investigation, we calculate the surface tension in the strong segregation limit, independent of any phase geometry.

KEY WORDS: Microphase separation; diblock copolymers; mean field theory; density functional theory.

1. INTRODUCTION

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

¹ Department of Mathematics, Simon Fraser University; e-mail: choksi@math.sfu.ca

² Department of Mathematics, Utah State University; e-mail: ren@math.usu.edu

stretching. Because of this energetic competition, a phase separation on a mesoscopic scale with A-rich 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 refs. 4 and 18). These ordered structures are key to the material properties which make diblock copolymers of great technological importance.

Various mean field theories have been introduced to model and capture aspects of the phase separation (see refs. 4 and 13 and the references therein). In particular, they have successfully predicted both the phase diagram as well as scaling laws for the length scale of the separation. In all these theories, one must accurately sum the competing energetic contributions of the interaction energy and elastic energy due to chain stretching. The latter is usually modeled via a phase space for the n polymer chains (continuous function curves) which is equipped with a product measure consisting of n -copies of Wiener measure; therefore highly coiled chains are favored over straight ones. With this state space, one introduces a Hamiltonian based upon the monomer interactions. At this point approximations must be made as seeking the Gibbs canonical distribution and the free energy is far too complicated due to the interactions between the copolymer chains. One of the most successful “approximate” theories is the self-consistent mean field theory (SCMFT) developed and applied over the years by several researchers including Leibler, Helfand, Wasserman, Hong, Noolandi, Matsen, and Schick (cf. refs. 23, 25–28, 30, 35). Here one simulates the effect of monomer interactions via external fields acting separately on the A and B monomers. Approximations are used,³ allowing for the computation of the free energy via an integration over *external fields* and the macroscopic densities they generate. From this SCMFT, Matsen and Schick (ref. 35) introduced a spectral method which yields predictions with striking resemblances to experiments.

There are three dimensionless material parameters involved in the microphase separation: χ , the Flory–Huggins interaction parameter measuring the incompatibility of the two monomers; N , the index of polymerization measuring the number of monomers per macromolecule; and a , measuring 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

³ We view this approximation via a variational principle (cf. Proposition 3.1).

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. refs. 19–21) that the domain size scales like $\chi^{\frac{1}{6}} N^{\frac{2}{3}}$ where as the interfacial length scales like $\chi^{-\frac{1}{2}}$. We remark that most experiments take place at temperatures which place one in the intermediate segregation regime (cf. ref. 18).

In refs. 29 and 40, Ohta and Kawasaki derived a density functional theory⁴ (DFT) which uses several approximations to write the free energy exclusively in terms of the (averaged) macroscopic monomer density. This idea was first used by Leibler (ref. 30) who focused on the WSR. In the Ohta–Kawasaki DFT one is left with the following free energy of a single order parameter ψ measuring the difference between the average A and B monomer densities:

$$\begin{aligned}
 E(\psi) := & \int_{\Omega} |\nabla\psi|^2 dx + \chi \int_{\Omega} \mathcal{W}(\psi) dx \\
 & + \alpha \int_{\Omega} \int_{\Omega} (\psi(x) - m)(\psi(y) - m) G(x, y) dx dy, \quad (1.1)
 \end{aligned}$$

where $\Omega \subset \mathbf{R}^3$ is the physical domain of the melt, α is inversely proportional to N^2 , and \mathcal{W} is a double-well energy with zeroes at $\psi = \pm 1$ only. The average over Ω of order parameter ψ is constrained to equal m (thus $m = 2a - 1$). $G(x, y)$ is the Green's function of the Laplacian operator with the Neumann boundary condition. A similar functional to (1.1) has been studied by Bahiana and Oono (ref. 2), and Liu and Goldenfeld (ref. 32, see also Section 8.4 of ref. 16).⁵

Dividing the energy by χ and rescaling space to focus on the shape effects, one arrives at a nonlocal *Cahn–Hilliard-like* (cf. ref. 6) functional of the form

$$\begin{aligned}
 E_{\epsilon, \sigma}(\psi) := & \frac{\epsilon^2}{2} \int_D |\nabla\psi|^2 dx \\
 & + \int_D \mathcal{W}(\psi) dx + \frac{\sigma}{2} \int_D \int_D (\psi(x) - m)(\psi(y) - m) G(x, y) dx dy, \quad (1.2)
 \end{aligned}$$

⁴ Many other “density functional theories” have been proposed; see, for example, refs. 31 and 33 and the survey article.⁽¹³⁾ See also related work in refs. 47 and 48.

⁵ See also the recent work of Muratov.⁽³⁶⁾

where D is a domain of unit volume, ϵ represents the interfacial thickness (suitably rescaled) at the A and B monomer intersections, and σ is again inversely proportional to N^2 . The exact relationship between ϵ , σ and the parameters χ , N , a , $|\Omega|$ are given in Section 5. The average of ψ over D is again constrained to equal m . This form of the energy was first written by Nishiura and Ohnishi in ref. 37 who noted that the DFT of Ohta–Kawasaki provides an ideal setting for a deeper mathematical analysis. The main advantage for the application of more sophisticated mathematical tools is that they can help in addressing a generic criticism about the analysis of domain structures via the minimization of a free energy. This has been well articulated by Bates and Fredrickson in *Physics Today* (ref. 4) who, in the context of mean field theories for microphase separation of copolymers, noted that “*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.*”⁶

Recently there has been a series of mathematical articles on the minimization of (1.2), both from the perspective of the analysis of partial differential equations (refs. 31, 41–47), and based upon some *direct methods* (refs. 1, 7, and 8) which apply in any space dimension. These types of analysis can allow one to draw certain conclusions, such as scaling laws, without any pre-assigned bias for the domain structures: that is, they allow for an analysis of minimizing structures within the framework of *all* structures. These results seem encouraging in terms of building ansatz-free techniques which successfully capture properties for *minimizers* of (1.2).

Mathematical results pertaining to (1.2) can only be meaningful if they are complemented with an understanding of where this functional comes from, and perhaps more importantly, a framework for addressing the extent to which (1.2) captures the essential physics of the problem (even if it is only *qualitative* information which remains). Questions have remained regarding the validity of the functional (1.1) (and hence (1.2)). For example, where as this DFT has successfully predicted observed scaling laws in the SSR (domain size $\sim \chi^{\frac{1}{6}} N^{\frac{2}{3}}$), questions have been raised (ref. 18) as to its validity in the SSR where certain approximations are not rigorously valid. Ohta *et al.* (ref. 39) have argued that while the expression of the free energy (1.1) is approximate, there are many indications which suggest that the essential physics of the ordered phases is captured by this

⁶ There have recently been several attempts to address this criticism, see, for example, refs. 11 and 5.

model. Matsen and Bates have noted in ref. 34 that while this theory makes qualitatively accurate predictions, “*it is difficult to assess all the approximations in this DFT and others like it.*”

With these comments in mind, the purpose of the present article is two-fold:

1. Re-examine the derivation of the Ohta–Kawasaki DFT theory, clearly presenting it as an offspring of the well-established SCMFT and clearly identifying the approximations used.
2. Provide a derivation of Nishiura and Ohnishi’s nonlocal *Cahn–Hilliard-like* functional (1.2) which is accessible to applied mathematicians and clearly illustrates the connection to the fundamental material parameters χ , N , and a .

Notation. For clarity, we provide a brief summary of some of our notation.

- $\Omega \subset \mathbf{R}^3$ is the physical domain with volume $|\Omega|$ on which the melt lives and D is a normalized physical domain of unit volume. We use x, y, z to denote points in \mathbf{R}^3 with dx (or dy, dz) in reference to a volume integral.

- Fields with super and sub indices of A and B will be used to denote reference to the A and B monomers respectively. We often use k and m as variables taking on the values of either A or B .

- The index of polymerization is denoted by the integer N . For a copolymer chain parametrized by either τ or $t \in [0, N]$, we let $\mathcal{I}_A = [0, N_A]$ denote the interval occupied by the A -monomers and $\mathcal{I}_B = [N_A, N]$ denote the interval occupied by the B -monomers. We let $N_B := N - N_A$. The molecular weight of the A and B monomers are denoted by a and b respectively (hence, $a = N_A/N$, $b = N_B/N$ with $a + b = 1$).

- $r = (r_1, \dots, r_n)$ denotes an n -tuple of copolymer chains (continuous functions from $[0, N]$ to \mathbf{R}^3). Associated to these n -tuples is an n -product Wiener measure denoted by $d\mu$ (see Section 2 for a precise definition). $H(r)$ and $D(r)$ denote respectively the interaction Hamiltonian and the Gibbs canonical distribution associated with the interacting chains. Z denotes the associated partition function. See Section 2 for more detailed definitions.

- $U = (U^A, U^B)$ denotes an external field acting respectively on the A and B monomers, and $\langle \cdot \rangle_U$ denotes the expectation with respect to D_U , the Gibbs canonical distribution induced by U . For a field U acting at a point y , we define $U(y, t) = U^k$, if $t \in \mathcal{I}_k$.

- $\rho(x, r)$ will denote a microscopic monomer density field. $\langle \rho \rangle_U$, u and ψ will denote different macroscopic density fields. An exception to this

convention will be in the second half of Section 4 where for convenience we temporarily use just $\rho(x)$ to denote the macroscopic density field.

- V^{AB}, V^{AA} , and V^{BB} denote the monomer interaction parameters and χ is the Flory–Huggins interaction parameter given by (4.22).

- l (NOT $a!$) denotes the Kuhn statistical length. The Boltzmann constant has been normalized to unity and β denotes the reciprocal of the absolute temperature measured in units of (energy)⁻¹.

- W and \mathcal{W} will denote double-well potentials for the macroscopic monomer density fields. F, I , and E will denote free energies for certain order parameters.

- Finally, the summation convention of matching super and sub indices is frequently used over A and B . For example,

$$d_k e^k := \sum_{k=A, B} d_k e^k, \quad d_{km} e^k f^m := \sum_{k=A, B} \sum_{m=A, B} d_{km} e^k f^m.$$

2. INTERACTING MOLECULAR CHAINS

The statistical physics of block copolymers is built on the fundamental work of de Gennes,⁽⁹⁾ Edwards,⁽¹²⁾ and Lifshitz.⁽¹⁷⁾ A single ideal chain r_1 of N total monomers is a Brownian process in the function space

$$\Gamma_1 = C([0, N], \mathbf{R}^3).$$

If we write every $r_1 \in C([0, N], \mathbf{R}^3)$ as $r_1 = r_1(0) + (r_1 - r_1(0))$, the space is decomposed into

$$C([0, N], \mathbf{R}^3) \equiv \mathbf{R}^3 \times \{r_1 \in C([0, N], \mathbf{R}^3) : r_1(0) = \vec{0}\}.$$

Let $dP_{\vec{0}}$ be the Wiener measure of the standard Brownian motion, scaled by a factor $l/\sqrt{3}$, on $\{r_1 \in C([0, N], \mathbf{R}^3) : r_1(0) = \vec{0}\}$. l is the Kuhn statistical length^(9,17) that measures the average distance between two adjacent monomers. In this paper we only consider the situation when this l is independent of the types of the adjacent monomers. $P_{\vec{0}}$ reminds us the probabilistic origin of this measure and the fact that $r_1(0) = \vec{0}$. This Wiener measure is often written formally as

$$dP_{\vec{0}} \sim \exp\left(-\frac{3}{2l^2} \int_0^N \left(\frac{dr_1(\tau)}{d\tau}\right)^2 d\tau\right) dr_1.$$

Then the space $C([0, N], \mathbf{R}^3)$ is equipped with the measure

$$d\mu_1 = dx \times dP_{\vec{0}}.$$

The A (B respectively) monomers occupy the interval $(0, N_A)$ ((N_A, N) respectively).

With n chains in the material, the phase space is

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

equipped with the product measure

$$d\mu = \underbrace{d\mu_1 \times d\mu_1 \times \dots \times d\mu_1}_n.$$

Were quantum indistinguishability effect taken into consideration, we would include a factor of $1/n!$ in this measure. It would also address the issue of extensivity of the system. In this paper we will not need this factor.

An external potential

$$\mathcal{P}_\Omega(x) = \begin{cases} 0, & x \in \Omega \\ \infty, & x \notin \Omega \end{cases}$$

exists to confine the molecules in $\Omega \subset \mathbf{R}^3$. With n chains of polymerization index N , there are nN monomers. Inside Ω the average monomer number density is $\rho_0 = nN/|\Omega|$. The interaction between monomers gives another two particle energy term so the Hamiltonian, ignoring the nonessential kinetic energy, takes the form

$$H(r) = \sum_{i,j} \sum_{k,m} \frac{V^{km}}{2\rho_0} \int_{\mathcal{J}_k} \int_{\mathcal{J}_m} \delta(r_i(\tau) - r_j(t)) d\tau dt + \sum_i \int_0^N \mathcal{P}_\Omega(r_i(\tau)) d\tau. \quad (2.1)$$

Here we assume that the interaction is short ranged in the use of the δ -function, and repulsive by taking $V^{km} > 0$. We deliberately use the super index for V^{km} for the practice of the summation convention later. This also indicates a conjugacy relation between the energy and the number density defined in (2.2). The Gibbs canonical distribution is

$$D(r) = \frac{1}{Z} \exp(-\beta H(r)), \quad Z = \int_\Gamma \exp(-\beta H(r)) d\mu$$

which describes the thermal equilibrium. Here we use the energy unit to measure the absolute temperature so the Boltzmann constant is 1 and β is the reciprocal of the absolute temperature. Note that the free energy of the system is $-\beta^{-1} \log Z$.

If we define the microscopic density fields

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

then under this distribution the expectations

$$\langle \rho_k(x) \rangle = \int_{\Gamma} \rho_k(x, r) D(r) d\mu, \quad k = A, B \quad (2.2)$$

give the macroscopic densities of the monomer units. In terms of $\rho_k(x, r)$ the Hamiltonian (2.1) becomes

$$H(r) = \int_{\Omega} \frac{V^{km}}{2\rho_0} \rho_k(x, r) \rho_m(x, r) dx.$$

3. THE SELF-CONSISTENT MEAN FIELD THEORY

It is hopeless to find $\langle \rho_k(x) \rangle$ directly from D due to the complexity of the interaction V . However D satisfies a variational principle (cf. ref. 3, Vol. 1, Section 4.2.2):

Proposition 3.1. For any other distribution D' (i.e., $D' \neq D$),

$$\beta \int_{\Gamma} H(r) D'(r) d\mu - S(D') > -\log Z.$$

If D' is replaced by D on the left side, the inequality becomes an equality.

Here $S(D')$ denotes the statistical entropy associated with the distribution D' , i.e.,

$$S(D') = - \int D' \log D' d\mu.$$

An approximation method comes into play based on Proposition 3.1. Consider a smaller class of distributions D' , and define

$$F(D') = \int_{\Gamma} H(r) D'(r) d\mu - \beta^{-1} S(D').$$

$F(D')$ may be considered as an approximate free energy of the original system under D' . Assume that in the smaller class $F(D')$ is easier to compute and minimize. Then the minimizer within this smaller class approximates the true distribution D .

In the self-consistent field theory (see Helfand,⁽²³⁾ Helfand and Wasserman,⁽²⁵⁻²⁷⁾ Hong and Noolandi,⁽²⁸⁾ Matsen and Schick⁽³⁵⁾—the latter two being formulated in the context of diblock copolymers), we choose the

class of distributions to be those generated by a pair of external fields $U = (U^A, U^B)$, acting on the A and B monomers respectively. There is no interaction between the monomers. We assume that

$$\sum_k \frac{\mathcal{J}_k}{N} \int_{\Omega} U^k(x) dx = 0. \quad (3.1)$$

The condition (3.1) may be achieved by adding a suitable constant to all U^k . The addition of such an overall constant only introduces an additive constant in the energy and does not affect the Gibbs canonical distribution that U induces. We impose the restriction that for every $x \notin \Omega$, $U^k(x) = \infty$ ($k = A, B$), to accommodate \mathcal{P}_{Ω} . The Hamiltonian on Γ of such a system is

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

It induces a Gibbs canonical distribution

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

We use $\langle \cdot \rangle_U$ to denote the expectation with respect to $D_U(r) d\mu$. Clearly if $x \notin \Omega$, $\langle \rho_k(x) \rangle_U = 0$.

The average internal energy under D_U is

$$\langle H \rangle_U := \int_{\Gamma} H(r) D_U(r) d\mu = \int_{\Omega} \frac{V^{km}}{2\rho_0} \langle \rho_k(x) \rangle_U \langle \rho_m(x) \rangle_U dx. \quad (3.2)$$

The entropy of D_U is

$$\begin{aligned} S(D_U) &= \log Z_U - \beta \frac{\partial}{\partial \beta} \log Z_U \\ &= \log Z_U + \frac{\beta}{Z_U} \int_{\Gamma} \exp(-\beta H_U(r)) \left[\sum_{i,k} \int_{\mathcal{J}_k} U^k(r_i(\tau)) d\tau \right] d\mu \\ &= \log Z_U + \beta \int_{\Gamma} \left[\sum_{i,k} \int_{\mathcal{J}_k} U^k(r_i(\tau)) d\tau \right] D_U(r) d\mu \\ &= \log Z_U + \beta n \int_{\Gamma} \left[\sum_k \int_{\mathcal{J}_k} U^k(r_1(\tau)) d\tau \right] D_U(r) d\mu \\ &= \log Z_U + \beta \int_{\Omega} U^k(x) \langle \rho_k(x) \rangle_U dx \end{aligned} \quad (3.3)$$

We now regard the approximate free energy F as a functional of the external fields $U = (U^A, U^B)$.

$$F(U) = \int_{\Omega} \left[\frac{V^{km}}{2\rho_0} \langle \rho_k(x) \rangle_U \langle \rho_m(x) \rangle_U - U^k(x) \langle \rho_k(x) \rangle_U \right] dx - \frac{1}{\beta} \log Z_U. \quad (3.4)$$

Note that only $\int_{\Gamma} H(r) D_U(r) d\mu$ relates the artificial external fields to the real interaction V .

The calculation of $F(U)$ is done by the Feynman–Kac integration theory (See ref. 15, Chap. 6). We note that because of the presence of \mathcal{P}_{Ω} that confines the molecules in Ω , $U^k(x) = \infty$ if $x \notin \Omega$. Therefore the Dirichlet boundary condition on $\partial\Omega \times (0, N)$ is imposed on the backward and forward parabolic partial differential equations associated with the Feynman–Kac integration theory. Let $Q_U(y, \tau, z, t)$ be the fundamental solution of the backward equation

$$(Q_U)_{\tau} + (l^2/6) \Delta_y Q_U - \beta U Q_U = 0, \quad Q_U(y, t, z, t) = \delta(y - z),$$

where $U(y, \tau) = U^k(y)$ if $\tau \in \mathcal{I}_k$ ($k = A, B$). Set q_U to be the solution of

$$(q_U)_{\tau} + (l^2/6) \Delta q_U - \beta U q_U = 0, \quad q_U(y, N) = 1, \quad (y, \tau) \in \Omega \times (0, N)$$

and q_U^* to be the solution of the forward equation

$$(q_U^*)_{\tau} - (l^2/6) \Delta q_U^* + \beta U q_U^* = 0, \quad q_U^*(y, 0) = 1, \quad (y, \tau) \in \Omega \times (0, N).$$

Note that

$$q_U(y, \tau) = \int_{\Omega} Q_U(y, \tau, z, N) dz, \quad q_U^*(y, \tau) = \int_{\Omega} Q_U(z, 0, y, \tau) dz.$$

Using the probabilistic notation so E_y is the expectation conditioned on $r_1(0) = y$, we find the partition function under U

$$\begin{aligned} Z_U &= \int_{\Gamma} \exp(-\beta H_U(r)) d\mu \\ &= \left\{ \int_{\Gamma_1} \exp\left(-\beta \sum_k \int_{\mathcal{I}_k} U^k(r_1(\tau)) d\tau\right) d\mu_1 \right\}^n \\ &= \left\{ \int_{\Omega} \left[E_y \exp\left(-\beta \sum_k \int_{\mathcal{I}_k} U^k(r_1(\tau)) d\tau\right) \right] dy \right\}^n \\ &= \left\{ \int_{\Omega} q_U(y, 0) dy \right\}^n = \left\{ \int_{\Omega} q_U^*(y, N) dy \right\}^n. \end{aligned}$$

Next we compute $\langle \rho_k(x) \rangle_U$.

$$\begin{aligned} \langle \rho_k(x) \rangle_U &= \frac{1}{Z_U} \int_{\Gamma} \left[\sum_i \int_{\mathcal{J}_k} \delta(r_i(\tau) - x) d\tau \right] \exp(-\beta H_U(r)) d\mu \\ &= \frac{n}{Z_U^{1/n}} \int_{\Gamma_1} \left[\int_{\mathcal{J}_k} \delta(r_1(\tau) - x) d\tau \right] \exp\left(-\beta \sum_k \int_{\mathcal{J}_k} U^k(r_1(\tau)) d\tau\right) d\mu_1 \\ &= \frac{n}{Z_U^{1/n}} \int_{\Omega} \left\{ E_y \int_{\mathcal{J}_k} \delta(r_1(\tau) - x) d\tau \exp\left(-\beta \int_0^N U(r_1(\tau), \tau) d\tau\right) \right\} dy \end{aligned}$$

For any fixed $\tau \in \mathcal{J}_k$,

$$\begin{aligned} &E_y \left\{ \delta(r_1(\tau) - x) \exp\left(-\beta \int_0^N U(r_1(t), t) dt\right) \right\} \\ &= E_y \left\{ \delta(r_1(\tau) - x) \exp\left(-\beta \int_0^\tau U(r_1(t), t) dt\right) \right. \\ &\quad \left. \times E_{r_1(\tau)} \exp\left(-\beta \int_\tau^N U(r_1(t), t) dt\right) \right\} \\ &= E_y \left\{ \delta(r_1(\tau) - x) \exp\left(-\beta \int_0^\tau U(r_1(t), t) dt\right) q_U(r_1(\tau), \tau) \right\} \\ &= q_U(x, \tau) E_y \left\{ \delta(r_1(\tau) - x) \exp\left(-\beta \int_0^\tau U(r_1(t), t) dt\right) \right\} \\ &= q_U(x, \tau) Q_U(y, 0, x, \tau). \end{aligned}$$

After integrating over y and τ we obtain

$$\langle \rho_k(x) \rangle_U = \frac{n}{Z_U^{1/n}} \int_{\mathcal{J}_k} q_U(x, \tau) q_U^*(x, \tau) d\tau. \quad (3.5)$$

This way Z_U , $\langle \rho_k(x) \rangle_U$, and most importantly $F(U)$ may be computed.

4. ORDER PARAMETERS $\langle \rho_k(x) \rangle$ AND THE DFT

In the expression $F(U) = \langle H \rangle_U - \beta^{-1} S(D_U)$ the $\langle H \rangle_U$ term (3.2) depends on U^k through $\langle \rho_k(x) \rangle_U$. We naturally take $\langle \rho_k(x) \rangle_U$ as order parameters, and invert (3.5) to express U^k and eventually F in terms of $\langle \rho_k(x) \rangle_U$. This idea was used in Leibler.⁽³⁰⁾

To turn the $-\beta^{-1} S(D_U)$ term in F as a functional of $\langle \rho_k(x) \rangle_U$ we will do some simplification. We start with calculating the derivative of F at

$U: \phi \rightarrow F'(U) \phi$ where $\phi = (\phi^A, \phi^B)$. It is done by differentiating the free energy of the perturbation $U^k + \epsilon \phi^k$ with respect to ϵ . Defining $\phi(y, t)$ the way that $U(y, t)$ is defined, we set p and p^* to be the solutions of

$$\begin{aligned} p_\tau + (l^2/6) \Delta p - \beta U p &= \beta \phi q_U, & p(x, N) &= 0, \\ p_\tau^* - (l^2/6) \Delta p^* + \beta U p^* &= -\beta \phi q_U^*, & p^*(x, 0) &= 0 \end{aligned} \quad (4.1)$$

which can be written as

$$\begin{aligned} p(x, \tau) &= -\beta \int_\tau^N \int_\Omega Q_U(x, \tau, y, t) q_U(y, t) \phi(y, t) dy dt \\ p^*(x, \tau) &= -\beta \int_0^\tau \int_\Omega Q_U(y, t, x, \tau) q_U^*(y, t) \phi(y, t) dy dt. \end{aligned}$$

Then we deduce

$$\begin{aligned} \frac{d(-\log Z_{U+\epsilon\phi})}{d\epsilon, \epsilon=0} &= -\frac{n}{Z_U^{1/n}} \frac{\partial}{\partial \epsilon, \epsilon=0} \int_\Omega q_{U+\epsilon\phi}(y, 0) dy \\ &= -\frac{n}{Z_U^{1/n}} \int_\Omega p(y, 0) dy \\ &= \frac{\beta n}{Z_U^{1/n}} \int_\Omega \int_0^N q_U(z, \tau) q_U^*(z, \tau) \phi(z, \tau) dt dz \\ &= \beta \int_\Omega \langle \rho_k(z) \rangle_U \phi^k(z) dz. \end{aligned} \quad (4.2)$$

Moreover

$$\begin{aligned} \frac{d}{d\epsilon, \epsilon=0} (-\beta) \int_\Omega (U + \epsilon\phi)^k(x) \langle \rho_k(x) \rangle_{U+\epsilon\phi} dx \\ = -\beta \int_\Omega \langle \rho_k(x) \rangle_U \phi^k(x) dx - \beta \int_\Omega U^k(x) \frac{\partial \langle \rho_k(x) \rangle_{U+\epsilon\phi}}{\partial \epsilon, \epsilon=0} dx. \end{aligned}$$

Therefore

$$\frac{d(-S(D_{U+\epsilon\phi}))}{d\epsilon, \epsilon=0} = -\beta \int_\Omega U^k(x) \frac{\partial \langle \rho_k(x) \rangle_{U+\epsilon\phi}}{\partial \epsilon, \epsilon=0} dx.$$

On the other hand we have

$$\frac{d\langle H \rangle_{U+\epsilon\phi}}{d\epsilon, \epsilon=0} = \int_{\Omega} \frac{V^{km}}{\rho_0} \langle \rho_k(x) \rangle_U \frac{\partial \langle \rho_m(x) \rangle_{U+\epsilon\phi}}{\partial \epsilon, \epsilon=0} dx,$$

and hence

$$F'(U) \phi = \int_{\Omega} \left(\frac{V^{km}}{\rho_0} \langle \rho_m(x) \rangle_U - U^k(x) \right) \frac{\partial \langle \rho_k(x) \rangle_{U+\epsilon\phi}}{\partial \epsilon, \epsilon=0} dx.$$

So it all comes down to finding

$$\begin{aligned} \frac{\partial \langle \rho_k(x) \rangle_{U+\epsilon\phi}}{\partial \epsilon, \epsilon=0} &= -Z_U^{-\frac{1+n}{n}} \frac{\partial Z_{U+\epsilon\phi}}{\partial \epsilon, \epsilon=0} \int_{\mathcal{J}_k} q_U(x, \tau) q_U^*(x, \tau) d\tau \\ &\quad + \frac{n}{Z_U^{1/n}} \int_{\mathcal{J}_k} (p(x, \tau) q_U^*(x, \tau) + p^*(x, \tau) q_U(x, \tau)) d\tau \\ &= \frac{\beta \langle \rho_k(x) \rangle_U}{n} \int_{\Omega} \langle \rho_m(y) \rangle_U \phi^m(y) dy \\ &\quad + \frac{n}{Z_U^{1/n}} \int_{\mathcal{J}_k} (p(x, \tau) q_U^*(x, \tau) + p^*(x, \tau) q_U(x, \tau)) d\tau. \end{aligned} \quad (4.3)$$

At this point, one easily derives the *self-consistent equations* (cf. ref. 35).⁷

⁷ Traditionally the diblock copolymer is assumed incompressible, i.e.,

$$\langle \rho_A(x) \rangle_U + \langle \rho_B(x) \rangle_U = \rho_0, \quad \forall x \in \Omega. \quad (4.4)$$

Under this constraint, any extremal of F satisfies the Euler–Lagrange equation

$$\frac{\delta F}{\delta U} = \frac{\delta}{\delta U} \int_{\Omega} \lambda(x) \sum_k \langle \rho_k(x) \rangle_U dx,$$

where $\lambda(x)$ is the Lagrange multiplier from (4.4). The earlier calculation of $F'(U) \phi$ yields

$$\int_{\Omega} \left(\frac{V^{km}}{\rho_0} \langle \rho_m(x) \rangle_U - U^k(x) \right) \frac{\partial \langle \rho_k(x) \rangle_{U+\epsilon\phi}}{\partial \epsilon, \epsilon=0} dx = \int_{\Omega} \lambda(x) \sum_k \frac{\langle \rho_k(x) \rangle_{U+\epsilon\phi}}{\partial \epsilon, \epsilon=0} dx.$$

We see that a sufficient condition for the equation to hold is

$$\frac{V^{km}}{\rho_0} \langle \rho_m(x) \rangle_U - U^k(x) = \lambda(x), \quad k = A, B. \quad (4.5)$$

The two equations in (4.5) constitute two of the five *self-consistent equations*. The other three are (3.5) (for $k = A, B$) and the incompressibility (4.4). In these five equations there are five unknown functions: $\langle \rho_A \rangle_U$, $\langle \rho_B \rangle_U$, U^A , U^B , and λ .

The Eqs. (4.2) and (3.3) imply that $-S(D_U)$ as a functional of $\langle \rho \rangle_U$ is the Legendre transform of $-\log Z_U$ as a functional of βU . This is consistent with the conjugacy relation between $\langle \rho \rangle_U$ and βU . Consequently

$$\frac{\delta(-S(D_U))}{\delta(\langle \rho \rangle_U)} = -\beta U. \quad (4.6)$$

So if we can express βU in terms of $\langle \rho \rangle_U$, then by integrating βU with respect to $\langle \rho \rangle_U$, we find $S(D_U)$.

We first study the reversed relation of $\langle \rho \rangle_U$ as a function of βU . Here we employ one of the several approximation steps in the paper. We linearize this dependence around $\beta = 0$,⁸ i.e.,

$$\langle \rho_k(x) \rangle_U \approx \langle \rho_k(x) \rangle_0 + \frac{\partial \langle \rho_k(x) \rangle_{0+\epsilon U}}{\partial \epsilon} \Big|_{\epsilon=0}. \quad (4.7)$$

This linearization will lead to $S(D_U)$ as a quadratic functional of $\langle \rho \rangle_U$. We compute from (3.5) as in (4.2) and (4.3),

$$\begin{aligned} & \frac{\partial \langle \rho_k(x) \rangle_{\epsilon U}}{\partial \epsilon} \Big|_{\epsilon=0} \\ &= -Z_0^{-\frac{1+n}{n}} \frac{\partial Z_{\epsilon U}}{\partial \epsilon} \Big|_{\epsilon=0} \int_{\mathcal{J}_k} q_0(x, \tau) q_0^*(x, \tau) d\tau \\ & \quad + \frac{n}{Z_0^{1/n}} \int_{\mathcal{J}_k} (p(x, \tau) q_0^*(x, \tau) + p^*(x, \tau) q_0(x, \tau)) d\tau \\ &= \frac{\langle \rho_k(x) \rangle_0}{n} \int_{\Omega} \langle \rho_m(y) \rangle_0 \beta U^m(y) dy \\ & \quad + \frac{n}{Z_0^{1/n}} \int_{\mathcal{J}_k} (p(x, \tau) q_0^*(x, \tau) + p^*(x, \tau) q_0(x, \tau)) d\tau. \end{aligned} \quad (4.8)$$

Note that in the above context, $p(x, \tau)$ is the solution to (4.1) wherein “the U ” is taken to be 0 and “the ϕ ” is taken to be U (cf. (4.3)).

Next we use another approximation: the thermodynamic limit of the system. We assume $\Omega \rightarrow \mathbf{R}^3$, the entire space, and $n \rightarrow \infty$ while keeping

⁸ See the Discussion of Section 6.

$\frac{n}{|\Omega|} = \frac{\rho_0}{N}$ unchanged in the process. This approximation is justified by the fact that $|\Omega|^{1/3} \gg l$. In this limit, we have

$$Q_0(y, \tau, z, N) \rightarrow \mathcal{H}(y-z, \tau-t) := \left(\frac{4\pi l^2 |\tau-t|}{6} \right)^{-3/2} \exp\left(-\frac{6|y-z|^2}{4l^2 |\tau-t|} \right), \quad (4.9)$$

where \mathcal{H} is the heat kernel on \mathbf{R}^3 . Consequently

$$q_0 \quad \text{and} \quad q_0^* \rightarrow 1, \quad \frac{n}{Z^{1/n}} \rightarrow \frac{\rho_0}{N}, \quad \langle \rho_k(x) \rangle_0 \rightarrow \bar{\rho}_k := \frac{N_k \rho_0}{N}. \quad (4.10)$$

By (3.1) we deduce

$$\frac{\langle \rho_k(x) \rangle_0}{n} \int_{\Omega} \langle \rho_m(y) \rangle_0 \beta U^m(y) dy \rightarrow 0. \quad (4.11)$$

Moreover

$$p(x, \tau) \rightarrow - \int_{\tau}^N [\mathcal{H}(\cdot, \tau-t) * \beta U(\cdot, t)](x) dt, \quad (4.12)$$

$$p^*(x, \tau) \rightarrow - \int_0^{\tau} [\mathcal{H}(\cdot, \tau-t) * \beta U(\cdot, t)](x) dt.$$

Define

$$R_{km}(z) := \int_{\mathcal{J}_k} \int_{i_m} \mathcal{H}(z, \tau-t) dt d\tau. \quad (4.13)$$

Using (4.8)–(4.12), the linear approximation (4.7) becomes

$$\langle \rho_k \rangle_U \approx \bar{\rho}_m - \frac{\rho_0}{N} R_{km} * (\beta U^m). \quad (4.14)$$

Since the Fourier transform of \mathcal{H} is

$$\hat{\mathcal{H}}(\xi) := \int_{\mathbf{R}^3} \mathcal{H}(x, t) e^{-2\pi i \xi \cdot x} dx = \exp\left(-\frac{4\pi^2 l^2 |t| |\xi|^2}{6} \right),$$

the Fourier transform of R_{km} in (4.13) is

$$\hat{R}_{km}(\xi) = \begin{cases} 2 \left(\frac{2\pi l |\xi|}{\sqrt{6}} \right)^{-4} h \left(\frac{4\pi^2 l^2 |\xi|^2 N_k}{6} \right) & \text{if } k = m \\ \left(\frac{2\pi l |\xi|}{\sqrt{6}} \right)^{-4} g \left(\frac{4\pi^2 l^2 |\xi|^2 N_k}{6}, \frac{4\pi^2 l^2 |\xi|^2 N_m}{6} \right) & \text{if } k \neq m \end{cases}$$

where

$$h(s_1) = e^{-s_1} + s_1 - 1 \quad \text{and} \quad g(s_1, s_2) = (1 - e^{-s_1})(1 - e^{-s_2}).$$

To compute the inverse \hat{T} of \hat{R} we make the following approximation. This is the third approximation we use in this section. The long and short wave expansions

$$h(s_1) \approx s_1, \quad g(s_1, s_2) \approx 1 \quad \text{if } s_1, s_2 \gg 1$$

$$h(s_1) \approx \frac{s_1^2}{2} - \frac{s_1^3}{6}, \quad g(s_1, s_2) \approx \left(s_1 - \frac{s_1^2}{2} \right) \left(s_2 - \frac{s_2^2}{2} \right) \quad \text{if } s_1, s_2 \ll 1,$$

lead to

$$\hat{T}(\xi) \approx \frac{(2\pi l |\xi|)^2}{6N} K + \frac{6}{(2\pi l |\xi|)^2 N^3} L,$$

wherein setting $a = N_A/N$ and $b = N_B/N$,

$$K = \frac{1}{2} \begin{bmatrix} a^{-1} & 0 \\ 0 & b^{-1} \end{bmatrix}, \quad L = \frac{3}{2} \begin{bmatrix} a^{-2} & -(ab)^{-1} \\ -(ab)^{-1} & b^{-2} \end{bmatrix}. \quad (4.15)$$

This type of expansion of \hat{T} was first used in Ohta and Kawasaki.⁽⁴⁰⁾ Recall that our goal here is to invert the dependence of $\langle \rho_k \rangle_U$ on U . For convenience of notation, we temporarily set $\rho_k = \langle \rho_k \rangle_U$. After performing the inverse Fourier transform to \hat{T} and inverting (4.14), we find βU expressed in terms of ρ :

$$\beta U^k(x) \approx -\frac{N}{\rho_0} T^{km} (\rho_m - \bar{\rho}_m)(x), \quad (4.16)$$

where

$$T = \frac{l^2}{6N} (-\Delta) K + \frac{6}{l^2 N^3} (-\Delta)^{-1} L.$$

Note that the operator $-\Delta$ comes from the term $(2\pi |\xi|)^2$ and $(-\Delta)^{-1}$ from $1/(2\pi |\xi|)^2$.

Based upon (4.6), we integrate (4.16) to obtain⁹

$$\begin{aligned} & -S(D_U) + S(D_0) \\ & \approx \frac{N}{2\rho_0} \int_{\mathbf{R}^3} (T^{km}(\rho_k - \bar{\rho}_k))(\rho_m - \bar{\rho}_m) dx \\ & = \frac{1}{2\rho_0} \int_{\mathbf{R}^3} \left[\frac{l^2 K^{kk}}{6} |\nabla \rho_k|^2 + \frac{6L^{km}}{l^2 N^2} ((-\Delta)^{-1} (\rho_k - \bar{\rho}_k))(\rho_m - \bar{\rho}_m) \right] dx. \quad (4.17) \end{aligned}$$

Note that in completing the integration by parts above, we have neglected the boundary terms at infinity.

Finally we return from the thermodynamic limit on \mathbf{R}^3 to the bounded domain Ω . There are some choices of boundary conditions for $(-\Delta)^{-1}$ on a bounded Ω : The Dirichlet, the Neumann, and the periodic boundary conditions are the most obvious ones. They lead to different Green functions on Ω . However the interior of the material is not significantly affected by the choice of the boundary condition. Here we take the Neumann boundary condition as an example. Denote the Green function by $G(x, y)$. Then (4.17) becomes

$$\begin{aligned} -S(D_U) + S(D_0) & \approx \frac{1}{2\rho_0} \int_{\Omega} \left[\frac{l^2 K^{kk}}{6} |\nabla \rho_k(x)|^2 \right. \\ & \quad \left. + \frac{6L^{km}}{l^2 N^2} \left(\int_{\Omega} G(x, y) (\rho_k(y) - \bar{\rho}_k) dy \right) (\rho_m(x) - \bar{\rho}_m) \right] dx. \quad (4.18) \end{aligned}$$

⁹ Note that $(-\Delta)^{-1} (\rho_k - \bar{\rho}_k)$ can be written as an integral:

$$(-\Delta)^{-1} (\rho_k - \bar{\rho}_k)(x) = \int_{\mathbf{R}^3} \frac{\rho_k(y) - \bar{\rho}_k}{4\pi |x - y|} dy$$

where $\frac{1}{4\pi |x - y|}$ is the Green function of $-\Delta$ in space.

A more elegant way to express the above expression is to introduce the nonlocal operator¹⁰ $(-\Delta)^{-1/2}$; thus

$$\begin{aligned} & \int_{\Omega} \left[\int_{\Omega} G(x, y) (\rho_k(y) - \bar{\rho}_k) dy (\rho_m(x) - \bar{\rho}_m) \right] dx \\ &= \int_{\Omega} ((-\Delta)^{-1/2} (\rho_k - \bar{\rho}_k)) ((-\Delta)^{-1/2} (\rho_m - \bar{\rho}_m)) dx. \end{aligned}$$

Combining (3.2) to (3.4) with (4.18), we find after dropping the unimportant constant $S(D_0)$:

$$\begin{aligned} F(\rho) = \int_{\Omega} \left[\frac{l^2 K^{kk}}{12\beta\rho_0} |\nabla\rho_k|^2 + \frac{3L^{km}}{l^2 N^2 \beta\rho_0} (-\Delta)^{-\frac{1}{2}} (\rho_k - \bar{\rho}_k) (-\Delta)^{-\frac{1}{2}} (\rho_m - \bar{\rho}_m) \right. \\ \left. + \frac{V^{km}}{2\rho_0} \rho_k(x) \rho_m(x) \right] dx. \end{aligned} \quad (4.19)$$

To separate the size effect of Ω from the shape effect of Ω , we scale Ω to $D = \{x: |\Omega|^{1/3} x \in \Omega\}$, whose 3-dimensional Lebesgue measure is 1. In the mean time introduce relative densities $u_k(x) = \rho_k(|\Omega|^{1/3} x) / \rho_0$, and let $u = (u_A, u_B)^T$ and $\bar{u} = (\bar{u}_A, \bar{u}_B)^T$, where $\bar{u}_k := \int_D u_k(x) dx$ denotes the average of u_k . Hereinafter the superscript T denotes the transpose operation on a vector. The relative densities turn (4.19) to a dimensionless form for $I = \beta F / (\rho_0 |\Omega|)$ —the relative free energy per monomer:

$$\begin{aligned} I(u) = \int_D \left[\frac{l^2 K^{kk}}{12 |\Omega|^{2/3}} |\nabla u_k|^2 \right. \\ \left. + \frac{3L^{km} |\Omega|^{2/3}}{l^2 N^2} (-\Delta)^{-\frac{1}{2}} (u_k - \bar{u}_k) (-\Delta)^{-\frac{1}{2}} (u_m - \bar{u}_m) + W(u) \right] dx. \end{aligned} \quad (4.20)$$

Here W is defined by (4) below, The first and second terms in (4.20) form the entropy part of the free energy. Since the total number of A (B respectively) monomers in Ω is $nN_A = nNa$ (nNb respectively), we have the monomer number constraints

$$\bar{u}_A = a, \quad \bar{u}_B = b, \quad (a + b = 1). \quad (4.21)$$

¹⁰ Precisely, this is the square root of the inverse of

$$-\Delta: \{\eta \in W^{2,2}(\Omega) : \partial_\nu \eta = 0 \text{ on } \partial\Omega, \bar{\eta} = 0\} \rightarrow \{\theta \in L^2(\Omega) : \bar{\theta} = 0\}.$$

Here $\bar{\eta} = \frac{1}{|\Omega|} \int_{\Omega} \eta dx$ is the average of η and $\bar{\theta}$ is the average of θ . $\partial_\nu \eta$ is the outward normal derivative of η .

The W term comes from the internal energy (3.2): i.e.,

$$W(u) = \frac{\beta V^{km}}{2} u_k u_m.$$

The four entries of V are all positive. In general we assume that

$$\chi = \beta V^{AB} - (\beta/2)(V^{AA} + V^{BB}) > 0. \quad (4.22)$$

The constant χ is called the Flory–Huggins parameter^(9,17) in polymer science. It is positive because in a block copolymer, dislike monomers repel each other more than like ones do.

Traditionally one assumes that the material is incompressible in the sense

$$u_A(x) + u_B(x) = 1, \quad \forall x \in D. \quad (4.23)$$

This condition¹¹ may be viewed as a consequence of the assumption that

$$W(u) = \begin{cases} \frac{\beta V^{km}}{2} u_k u_m & \text{if } u_A + u_B = 1, \quad u_A \geq 0, \quad u_B \geq 0 \\ \infty & \text{otherwise.} \end{cases} \quad (4.24)$$

It is often more convenient to subtract a linear term from (4.24) so that W attains global minimum 0 at (1, 0) and (0, 1):

$$W(u) = \begin{cases} \frac{\beta V^{km}}{2} u_k u_m - \frac{\beta V^{kk}}{2} u_k & \text{if } u_A + u_B = 1, \quad u_A \geq 0, \quad u_B \geq 0 \\ \infty & \text{otherwise.} \end{cases} \quad (4.25)$$

Because of the constraints (4.21), subtracting a linear term from W only changes I by a constant, not affecting any minimization operation. This new W satisfies $W(u) \geq 0$ for all u and $W(u) = 0$ if and only if $u = (1, 0)$ or $u = (0, 1)$.

¹¹ Alternatively and perhaps more naturally, one may replace the hard incompressibility condition (4.23) with a soft condition: that is extend the function W from (4.25) to a function defined on \mathbf{R}^2 which satisfies (i) W is smooth on \mathbf{R}^2 . (ii) The second derivative matrices at (1, 0) and (0, 1) are positive definite. (iii) $W(u) \rightarrow \infty$ quadratically as $|u| \rightarrow \infty$.

5. THE OHTA-KAWASAKI AND NONLOCAL CAHN-HILLIARD-LIKE FUNCTIONAL

We now reduce to a scalar order parameter and derive the Ohta–Kawasaki functional (1.1) as well as the rescaled nonlocal *Cahn–Hilliard-like* functional (1.2). Because of the incompressibility constraint, we may work only with u_A (i.e., $u_B = 1 - u_A$). Using (4.15) with $a + b = 1$, we rewrite each term in (4.19) in terms of u_A and nondimensionalize as in (4.20). We obtain

$$I(u_A) = C_1 \int_{\Omega} |\nabla u_A|^2 dx + C_2 \int_{\Omega} (-\Delta)^{-\frac{1}{2}} (u_A - a) \cdot (-\Delta)^{-\frac{1}{2}} (u_A - a) dx + \int_{\Omega} W(u_A) dx, \quad (5.1)$$

where following (4.25) and (4.22), $W(u_A) = \chi u_A(1 - u_A)$ for $0 \leq u_A \leq 1$, and

$$C_1 = \frac{l^2}{24a(1-a)} \quad C_2 = \frac{9}{2l^2 N^2 a^2 (1-a)^2}.$$

Setting $\psi = u_A - u_B = 1 - 2u_A$ and $m = 1 - 2a$ we may rewrite I above in terms of ψ , without affecting the minimization process, obtaining essentially the Ohta–Kawasaki functional (1.1).

To derive (1.2) in terms of the order parameter ψ , we rescale space (as in (4.20)) to separate size effects from shape effects; normalizing the domain to unit volume. We also rescale the energy by $1/\chi$. We arrive at

$$E_{\epsilon, \sigma}(\psi) := \frac{\epsilon^2}{2} \int_D |\nabla \psi|^2 dx + \int_D \mathcal{W}(\psi) dx + \frac{\sigma}{2} \int_D \int_D (\psi(x) - m)(\psi(y) - m) G(x, y) dx dy, \quad (5.2)$$

where $\mathcal{W}(\psi) = \frac{1}{4}(1 - \psi^2)$ for $|\psi| \leq 1$, and the dimensionless quantities ϵ and σ are given by

$$\epsilon^2 = \frac{l^2}{3 a (1-a) \chi |\Omega|^{2/3}} \quad \sigma = \frac{36 |\Omega|^{2/3}}{a^2 (1-a)^2 l^2 \chi N^2}.$$

This is the form of the Ohta–Kawasaki functional first considered by Nishiura and Ohnishi (ref. 37). The parameter ϵ is a rescaled interfacial thickness, i.e.,

$$\epsilon |\Omega|^{1/3} = \frac{l}{\sqrt{3a(1-a) \chi}},$$

consistent with the fact that in the SSR, the interfacial thickness scales like $1/\sqrt{\chi}$.

We also remark that, neglecting the dependencies on a , the regime $\epsilon \ll \sigma$ is equivalent to $\chi^{1/6} N^{2/3} l \ll |\Omega|^{1/3}$. As previously noted, in the SSR both experiments and several models (including this DFT) predict that the domain size scales like $\chi^{1/6} N^{2/3} l$. Hence the latter inequality may be viewed as a self-consistency requirement enabling the formation of domains on this scale. In particular, working in the regime $\epsilon \ll \sigma$ places one in the SSR (cf. refs. 7, 37, and 41).

6. DISCUSSION

We have re-derived the Ohta–Kawasaki DFT from the statistical physics of interacting chains using the SCMFT as our starting point. This process involved several approximations. The first (cf. Proposition 3.1) is the basis for the SCMFT and amounts to replacing the true free energy stemming from the interacting monomers with the minimum over all fields U of the expression (3.4). This approximation is essentially equivalent to the more frequently used approximation whereby *functional integrals* are replaced with extremal values of the integrand. The latter process is often dubbed “the Random Phase Approximation” (cf. ref. 40). As mathematicians, we view the variational principle as more natural but, of course, are unable to determine the accuracy of this approximation.

The other three approximations come from the inversion process in Section 4, whereby all fields are calculated in terms of the order parameter $\langle \rho \rangle$. The basic step here is the linearization about $\beta = 0$ of the dependence of $\langle \rho \rangle_U$ on U . The accuracy is dependent on the size of β^{12} which is inversely proportional to temperature. Herein lies the skepticism for the application of this DFT in the SSR. Moreover, it is also difficult to assess its accuracy in the intermediate segregation regime wherein most experiments take place. As previously mentioned, this DFT does give accurate predictions for the domain size scaling law in the SSR. It would perhaps be more interesting to determine whether or not it can also predict all the observed structures in the weak and intermediate segregation regimes which were previously predicted by the SCMFT, for example the double-gyroid phase (cf. ref. 35). Very recently, Teramoto and Nishiura⁽⁴⁹⁾ used the Ohta–Kawasaki DFT to show numerically that within a very small parameter regime, energy minimization leads to the double gyroid phase. Ohta *et al.* have also recently implemented simulations of this phase (ref. 38).

¹² Note that β has dimensions of energy⁻¹. The associated units of energy are naturally those of the V^{km} (which are also the units of the external fields U^k). Thus small β means $\chi \ll 1$.

APPENDIX A

Here we calculate the interfacial energy associated with A - B monomer interfaces. We use the powerful notion of variational convergence (dubbed *Gamma-convergence*) which was introduced by Ennio De Giorgi (ref. 10). After a suitable rescaling in space, one is able to rigorously determine the asymptotic behavior (as the *relative* interfacial thickness tends to zero) of minimizers via the asymptotic behavior of the functionals they minimize. As a consequence of this procedure, the interfacial energy density (or surface tension) is determined in terms of the relevant material parameters. We will omit the details of the proof of *Gamma-convergence*, which may easily be inferred from a related result in ref. 44. The reader not familiar with this type of mathematical analysis (or the spaces BV and $W^{1,2}$) may either skip to formula (A.3) or see ref. 10 for more details. Our main point here is to illustrate that this technique allows one to calculate the surface tension without any a priori assumptions on the phase geometry.

We work with the vector-valued order parameter u and the free energy given by (4.20). We choose the size of Ω in a rather special way so that $|\Omega|^{1/3} \sim N^{2/3}l$. We introduce the following notation:

$$\varepsilon = \frac{l}{\sqrt{6} |\Omega|^{1/3}}, \quad \lambda = \frac{6\sqrt{6} |\Omega|}{l^3 N^2}. \quad (\text{A.1})$$

As a consequence $\lambda \sim 1$ is a fixed positive constant. This choice of $|\Omega|^{1/3}$ will later facilitate the use of the *Gamma-convergence* theory. Regarding ε we assume that $\varepsilon \rightarrow 0$, a consequence of $|\Omega|^{1/3} \sim N^{2/3}l$ and $N \rightarrow \infty$: Thus we are considering the strong segregation limit.

After rescaling space so that Ω transforms to a unit domain, I in (4.20) becomes a family of functionals parameterized by ε :

$$I_\varepsilon(u) = \int_D \left[\frac{\varepsilon^2}{2} K^{kk} |\nabla u_k|^2 + \frac{\varepsilon \lambda}{2} L^{km} (-\Delta)^{-\frac{1}{2}} (u_k - \bar{u}_k) (-\Delta)^{-\frac{1}{2}} (u_m - \bar{u}_m) + W(u) \right] dx. \quad (\text{A.2})$$

I_ε is initially defined on $X = \{(u_A, u_B)^T: u_A, u_B \in W^{1,2}(D), \bar{u}_A = a, \bar{u}_B = b\}$ but for technical reasons we extend its domain to $\hat{X} = \{(u_A, u_B)^T: u_A, u_B \in L^2(D), \bar{u}_A = a, \bar{u}_B = b\}$, by trivially setting $I_\varepsilon(u) = \infty$ if $u \in \hat{X} \setminus X$. One can prove that minimizers of $\varepsilon^{-1}I_\varepsilon$ (and their energies) converge to minimizers (and their respective energies) of a sharp interface variational

problem involving the functional J . This is accomplished, in part, by proving that $\varepsilon^{-1}I_\varepsilon$ Gamma-converges to J . The functional J is defined by:

$$J(u) = \gamma_{AB} \|D1_{E_u}\| (D) + \frac{\lambda}{2} \int_D L^{km} (-\Delta)^{-\frac{1}{2}} (u_k - \bar{u}_k) (-\Delta)^{-\frac{1}{2}} (u_m - \bar{u}_m) dx,$$

if u is in

$$X_0 = \{(u_A, u_B)^T \in \hat{X} : u_A, u_B \in BV(D), (u_A, u_B) = (1, 0) \text{ or } (0, 1) \text{ a.e.}\}$$

and $J(u) = \infty$ if $u \in \hat{X} \setminus X_0$. 1_{E_u} is the characteristic function of the set $E_u := \{x \in D : u(x) = (1, 0)\}$. Since it has bounded variation, its derivative $D1_{E_u}$ is a vector of two signed measures. The total variation of the two measures is the positive measure $\|D1_{E_u}\|$. In particular, $\|D1_{E_u}\| (D)$ is simply the total surface area of interface between the A and B domains. The constant γ_{AB} (the surface tension) is defined by

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

where $A = \{\eta \in C^1([0, 1], \mathbf{R}^2) : \eta(0) = (1, 0)^T, \eta(1) = (0, 1)^T\}$. To interpret γ_{AB} in terms of βV^{km} in (4.25), we note that the optimal choice of $\eta(t)$ is $\eta(t) = (1, 0)^T (1-t) + (0, 1)^T t$. The function W we use is (4.25). From these η and W we deduce

$$\gamma_{AB} = \left(\int_0^1 \sqrt{(1-t)t} dt \right) \sqrt{\chi \left(\frac{1}{a} + \frac{1}{1-a} \right)} = \frac{\pi}{8} \sqrt{\frac{\chi}{a(1-a)}}. \quad (A.3)$$

Note that it is the Flory–Huggins parameter χ which appears in γ_{AB} .

If we return to the original sample Ω and recall $I = \beta F / (\rho_0 |\Omega|)$, $\beta = 1/(kT)$ and (A.1), then (A.3) implies that the interfacial free energy per unit area is

$$\frac{\rho_0 l k T}{\sqrt{6}} \frac{\pi}{8} \sqrt{\frac{\chi}{a(1-a)}}. \quad (A.4)$$

In Helfand and Tagami⁽²⁴⁾ the interfacial free energy is calculated from the self-consistent mean field theory. The result there is

$$\sqrt{\frac{\chi}{6}} \rho_0 l k T. \quad (A.5)$$

(A.5) does not involve a . Otherwise (A.4) and (A.5) differ by a numerical factor.

ACKNOWLEDGMENTS

We would like to thank Cyrill Muratov for useful discussions on the subject matter.

REFERENCES

1. G. Alberti, R. Choksi, and F. Otto, *Uniform Energy Distribution for Minimizers of a Nonlocal Functional Describing Microphase Separation of Diblock Copolymers*, in preparation.
2. M. Bahiana and Y. Oono, Cell dynamical system approach to block copolymers, *Phys. Rev. A* **41**:6763–6771 (1990).
3. R. Balian, *From Microphysics to Macrophysics: Methods and Applications of Statistical Physics*, Two Volumes (Springer-Verlag, Berlin, 1991).
4. F. S. Bates and G. H. Fredrickson, Block copolymers—designer soft materials, *Physics Today* **52**:32–38 (Feb, 1999).
5. Y. Bohbot-Raviv and Z.-G. Wang, Discovering new ordered phases of block copolymers, *Phys. Rev. Lett.* **85**:3428–3431 (2000).
6. J. W. Cahn and J. E. Hilliard, Free energy of a nonuniform system I. Interfacial free energy. *J. Chem. Phys.* **28**:258–267 (1958).
7. R. Choksi, Scaling laws in microphase separation of diblock copolymers, *J. Nonlinear Sci.* **11**:223–236 (2001).
8. R. Choksi, R. V. Kohn, and F. Otto, Domains branching in uniaxial ferromagnets: A scaling law for the minimum energy, *Comm. Math. Phys.* **201**:61–79 (1999).
9. P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, NY, 1979).
10. G. Dal Maso, *Introduction to Gamma-Convergence*, Progress in nonlinear differential equations and their applications, Vol. 8 (Birkhauser, Boston, 1993).
11. F. Drolet and G. H. Fredrickson, Combinatorial screening of complex block copolymer assembly with self-consistent field theory, *Phys. Rev. Lett.* **83**, 4317–4320 (1999).
12. S. F. Edwards, The theory of polymer solutions at intermediate concentration, *Proc. Phys. Soc. (London)* **88**:265–280 (1966).
13. G. H. Fredrickson, V. Ganesan, and F. Drolet, Field-theoretic computer simulation methods for polymer and complex fluids, *Macromolecules* **16** (2002).
14. P. Fife and D. Hilhorst, The Nishiura–Ohnishi free boundary problem in the 1D case, *SIAM J. Math. Anal.* **33**:589–606 (2001).
15. A. Friedman, *Stochastic Differential Equations and Applications*, Vol. 1 (Academic Press, New York, 1975).
16. N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group*, Frontiers in Physics (Addison–Wesley, 1992).
17. A. Y. Grosberg and A. R. Khokhlov, *Statistical Physics of Macromolecules* (American Institute of Physics (AIP) Press, New York, 1994).
18. I. W. Hamley, *The Physics of Block Copolymers* (Oxford Science Publications, 1998).
19. T. Hashimoto, M. Shibayama, and H. Kawai, Domain-boundary structure of styrene-isoprene block copolymer films cast from solution 4, molecular-weight dependence of lamellar microdomains, *Macromolecules* **13**:1237–1247 (1980).
20. T. Hashimoto, M. Shibayama, and H. Kawai, Ordered structure in block polymer solutions 4. Scaling rules on size of fluctuations with block molecular weight, concentration, and temperature in segregation and homogeneous regimes, *Macromolecules* **16**:1093–1101 (1983).

21. T. Hashimoto, M. Fujimura, and H. Kawai, Domain-boundary structure of styrene-isoprene block copolymer films cast from solution 5. Molecular-weight dependence of spherical microdomains, *Macromolecules* **13**:1660–1669 (1980).
22. T. Hashimoto, H. Tannaka, and H. Hasegawa, *Molecular Conformation and Dynamics of Macromolecules in Condensed Systems*, M. Nagasawa, ed. (Elsevier, Amsterdam, 1998).
23. E. Helfand, Theory of inhomogeneous polymers: Fundamentals of Gaussian random walk model, *J. Chem. Phys.* **62**:999–1005 (1975).
24. E. Helfand and Tagami, Theory of the interface between immiscible polymers II, *J. Chem. Phys.* **56**:3592–3601 (1972).
25. E. Helfand and Z. R. Wasserman, Block copolymer theory 4. Narrow interphase approximations, *Macromolecules* **9**:879–888 (1976).
26. E. Helfand and Z. R. Wasserman, Block copolymer theory 5. Spherical domains, *Macromolecules* **11**:960 (1978).
27. E. Helfand and Z. R. Wasserman, Block copolymer theory 6. Cylindrical domains, *Macromolecules* **13**:994–998 (1980).
28. K. M. Hong and J. Noolandi, Theory of inhomogeneous multicomponent polymer systems, *Macromolecules* **14**:727–736 (1981).
29. K. Kawasaki, T. Ohta, and M. Kohrogui, Equilibrium morphology of block copolymer melts 2, *Macromolecules* **21**:2972–2980 (1988).
30. L. Leibler, Theory of microphase separation in block copolymers, *Macromolecules* **13**:1602–1617 (1980).
31. R. L. Lescanec and M. Muthukumar, Density functional theory of phase transitions in diblock copolymer systems, *Macromolecules* **26**:3908–3916 (1993).
32. F. Liu and N. Goldenfeld, Dynamics of phase separation in block copolymer melts, *Phys. Rev. A* **39**:4805 (1989).
33. J. Malenkevitz and M. Muthukumar, Density functional theory of lamellar ordering in diblock copolymers, *Macromolecules* **24**:4199–4205 (1991).
34. M. W. Matsen and F. Bates, Unifying weak- and strong-segregation block copolymer theories, *Macromolecules* **39**:1091–1098 (1996).
35. M. W. Matsen and M. Schick, Stable and unstable phases of a diblock copolymer melt, *Phys. Rev. Lett.* **72**:2660–2663 (1994).
36. C. B. Muratov, Theory of domain patterns in systems with long-range interactions of coulomb type, *Phys. Rev. E* **66**:066108 (2002).
37. Y. Nishiura and I. Ohnishi, Some mathematical aspects of the micro-phase separation in diblock copolymers, *Physica D* **84**:31–39 (1995).
38. T. Ohta, personal communication.
39. T. Ohta, Y. Enomoto, J. Harden, and M. Doi, Anomalous rheological behavior of ordered phases of block copolymers I, *Macromolecules* **26**:4928–4934 (1993).
40. T. Ohta and K. Kawasaki, Equilibrium morphology of block copolymer melts, *Macromolecules* **19**:2621–2632 (1986).
41. I. Ohnishi, Y. Nishiura, M. Imai, and Y. Matsushita, Analytical solutions describing the phase separation driven by a free energy functional containing a long-range interaction term, *CHAOS* **9**:329–341 (1999).
42. X. Ren and J. Wei, On energy minimizers of the diblock copolymer problem, *Interfaces and Free Boundaries* **5**:193–238 (2003).
43. X. Ren and J. Wei, Concentrically layered energy equilibria of the di-block copolymer problem, *Eur. J. Appl. Math* **13**:479–496 (2002).
44. X. Ren and J. Wei, On the multiplicity of two nonlocal variational problems, *SIAM J. Math. Anal.* **31**:909–924 (2000).

45. X. Ren and J. Wei, On the spectra of 3-D lamellar solutions of the diblock copolymer problem, *SIAM J. Math. Anal.*, to appear.
46. X. Ren and J. Wei, Wriggled lamellar solutions and their stability in the diblock copolymer problem, preprint.
47. A. N. Semenov, Contributions to the theory of microphase layering in block-copolymer melts, *Sov. Phys. JETP* **61**:733–742 (1985).
48. A. N. Semenov, Microphase separation in diblock-copolymer melts: Ordering of micelles, *Macromolecules* **22**:2849–2851 (1989).
49. T. Teramoto and Y. Nishiura, Double gyroid morphology in a gradient system with nonlocal effects, *J. Phys. Soc. Japan* **71**:1611–1614 (2002).