

# Triblock Copolymer Theory: Free Energy, Disordered Phase and Weak Segregation

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## Abstract

We derive an order parameter model for triblock copolymers. After the statistical description of interacting polymer chains is presented, the self-consistent field theory is used as a variational approximation method to obtain a free energy minimization problem with respect to effective potential fields. We then identify the monomer densities under such fields as order parameters and view the free energy as a functional of these densities. This model is applied to study the disordered phase and the weak segregation phenomenon of the ordered phases.

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## 1 Introduction

Block copolymers belong to a class of soft materials that in contrast to crystalline solids, are characterized by fluid-like disorder on the molecular scale and a high degree of order at longer length scales. They are produced by joining two or more chemically distinct homopolymer blocks, each a linear series of identical monomers. The unlike monomers in the coil-like long chain molecules are thermodynamically incompatible. This results in microphase separation of monomer blocks on the molecular scale (5-100 nm) at low temperature, producing complex morphology structures or phases. Such structures give many desirable physical properties in application. For instance the polyurethane foams used in upholstery and bedding are composed of multi-block copolymers known as thermoplastic elastomers that combine high temperature resilience and low temperature flexibility.

Modern synthetic chemistry has “exposed fresh opportunities for using judicious combinations of multiple homopolymer blocks in novel molecular architectures to produce a seemingly unlimited number of exquisitely structured block copolymers endowed with tailored mechanical, optical, electrical, ionic, barrier, and other physical properties. Two decades of theoretical development have

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culminated in remarkably predictive statistical theories that can account for the domain shapes, dimensions, connectivity and ordered symmetry of many types of block copolymers” – Bates and Fredrickson [2].

One classifies block copolymers by the number of distinct monomer types. In a diblock copolymer there are two types of monomer units  $A$  and  $B$ . A diblock copolymer molecule is a chain of  $A$  monomer units linked chemically to a chain of  $B$  monomer units. For instance in the isoprene-styrene diblock copolymer,  $A =$  isoprene and  $B =$  styrene. In a triblock copolymer, such as isoprene-styrene-2vinylpyridine (see Mogi et al [19]), a molecule is a chain of  $A$  monomers, connected to a chain of  $B$  monomers, which is again connected to a chain of the third type  $C$  monomers. Triblock copolymers are new and, to the authors’ knowledge, industrial applications have yet to be found, although experimental studies have been done, e.g. [19]. This paper is devoted to some theoretical aspects of the triblock copolymer theory.

The monomer density fields of block copolymers are identified as the macroscopic quantities that describe the morphology structures, and in turn determine many other physical properties. The formation and evolution of these densities, together with the phase transitions between them, make up the central part of the block copolymer theory.

In this paper we re-examine an order parameter model for triblock copolymers, first derived by Nakazawa and Ohta [20]. It is a free energy expressed as a functional of the monomer density fields. The original functional (2.25) in [20] is stated on the entire space, with the help of the Fourier transform. In this paper we formulate it on a bounded domain in (5.1). This allows us to use mathematically rigorous methods to study various morphology phases. Using (5.1), we study the disordered phase in Section 6. In the disordered phase the monomer number densities are homogeneous. We identify the parameter range that corresponds to this phase. We mention the phenomenon of weak segregation, which occurs in an ordered phase of copolymers, but before strong segregation where a pattern of microdomains that are rich with one particular type of monomers is formed. The strong segregation phenomenon is studied in another paper [29]. There we find free energy local minimizers modeling the  $ABC$  lamellar phase.

In the literature the study of morphology phases are done by comparing the free energy of test density fields with various geometry. One may find a study of the lamellar, cylindrical, spherical, and diamond structures in [20], and the gyroid and double-diamond structures in Matsen [17]. This approach is not mathematically satisfactory since such test fields do not in general satisfy the Euler-Lagrange equation (5.9) of (5.1). Here we initiate a theoretical approach to solve the Euler-Lagrange equation. Moreover we will analyze the stability of the solutions, because only local minimizers of (5.1) are *meta-stable* states. This approach has been successful in analyzing the  $ABC$  lamellar phase of triblock copolymers [29], and the  $AB$  lamellar phase of diblock copolymers [26, 28]. There is also success in studying concentric ring pattern solutions for the diblock copolymer problem [27]. Such concentric ring pattern solutions may be viewed as *defects* of the lamellar phase. In these papers several mathematical techniques including  $\Gamma$ -convergence theory, energy comparison method, and rigorous singular perturbation analysis are applied.

We start in Section 2 with the statistical description of interacting polymer chains. In Section 3 we use the self-consistent field theory to derive a free energy minimization problem. Our approach to the self-consistent field theory differs from the ones in the literature (see Helfand [9], Helfand and Wasserman [10, 11, 12], Hong and Noolandi [14, 15]) in that we justify the theory by a variational principle, Proposition 3.1, for the Gibbs canonical distribution. We believe that this approach reveals more physical insight. For greater mathematical rigor we are also more careful about the role played by the shape and volume of the material.

The free energy minimization problem at this point, is a functional of the effective, self-consistent field. Numerical calculation was done by Matsen and Schick [18] for diblock copolymers to find such a field that best simulate the original interacting monomer chains. However it is still a mathematically difficult nonlocal minimization problem, especially for triblock copolymers. In Section 4 we identify the macro monomer densities under an effective field as order parameters, and as done in Leibler [16] and Ohta and Kawasaki [23] for diblock copolymers, and in [20] for triblock copolymers, convert the free energy as a functional of these order parameters. In this process we identify the three approximation steps: linearization of the density to mean field relation; the thermodynamic limit; and the long and short wave approximation. The final functional (5.1) is defined on a bounded region. It extends the one formulated for diblock copolymers by Nishiura and Ohnishi [21].

There have been few mathematical studies on triblock copolymers to this day. On the mathematical aspects of diblock copolymers there are [21], Ohnishi, et al [22], Ren and Wei [26, 24, 27, 28, 25], Fife and Hilhorst [6], Choksi [3], and Henry [13].

The summation convention of matching super and sub indices is frequently used over  $A, B, C$  in this paper. For instance

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

## 2 Interacting molecular chains

The statistical physics of block copolymers is built on the fundamental work of de Gennes [4], Edwards [5], and Lifshitz [8]. A single ideal chain  $r_1$  of total  $N$  monomers ( $N$  is called the polymerization index) is a Brownian process in the function space  $\Gamma_1 = C([0, N], R^3)$ . If we write every  $r_1 \in C([0, N], R^3)$  as  $r_1 = r_1(0) + (r_1 - r_1(0))$ , the space is decomposed into

$$\Gamma_1 \equiv R^3 \times \{r_1 \in C([0, N], R^3) : r_1(0) = \vec{0}\}. \quad (2.1)$$

Let  $d^3x$  be the Lebesgue measure on  $R^3$  and  $dP$  be the Wiener measure of the standard Brownian motion, scaled by a factor  $l/\sqrt{3}$ , on  $\{r_1 \in C([0, N], R^3) : r_1(0) = \vec{0}\}$ .  $l$  is the Kuhn statistical length [4, 8] 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 any adjacent monomers.  $P$  reminds us of the probabilistic origin of the Wiener measure. It is often written formally as

$$dP = \exp\left[-\frac{3}{2l^2} \int_0^N \left(\frac{dr_1(\tau)}{d\tau}\right)^2 d\tau\right] dr_1. \quad (2.2)$$

The space  $\Gamma_1$  is equipped with the measure  $d\mu_1 = d^3x \times dP$ . In each chain there are  $N_A$   $A$  monomers,  $N_B$   $B$  monomers and  $N_C$   $C$  monomers, so  $N_A + N_B + N_C = N$ . The  $A$  ( $B$  and  $C$  respectively) monomers occupy the interval  $i_A = (0, N_A)$  ( $i_B = (N_A, N_A + N_B)$  and  $i_C = (N_A + N_B, N)$  respectively).

With  $n$  chains in the material, the phase space is

$$\Gamma = \underbrace{\Gamma_1 \times \Gamma_1 \times \dots \times \Gamma_1}_n \quad (2.3)$$

on which is the product measure

$$d\mu = \underbrace{d\mu_1 \times d\mu_1 \times \dots \times d\mu_1}_n. \quad (2.4)$$

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  $V_\Omega(x)$ , which is 0 if  $x \in \Omega$  or  $\infty$  if  $x \notin \Omega$ , exists to confine the molecules in  $\Omega \subset R^3$ . With  $n$  chains of polymerization index  $N$ , there are  $nN$  monomers. Inside  $\Omega$  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

$$H(r) = \sum_{i,j} \sum_{k,m} \frac{V^{km}}{2\rho_0} \int_{i_k} \int_{i_m} \delta(r_i(\tau) - r_j(t)) d\tau dt + \sum_i \int_0^N V_\Omega(r_i(\tau)) d\tau, \quad (2.5)$$

where  $i$  and  $j$  range over  $1, 2, \dots, n$ , and  $k$  and  $m$  over  $A, B, C$ . We assume that the interaction is short ranged in the use of the  $\delta$ -function, and repulsive by taking  $V^{km} > 0$ .  $V^{km}$  is symmetric, i.e.  $V^{km} = V^{mk}$ ,  $\forall k, m \in \{A, B, C\}$ . 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 (2.9). Three Flory-Huggins parameters  $\chi^{AB}$ ,  $\chi^{BC}$  and  $\chi^{CA}$  [4, 8] are defined in terms of  $V^{km}$ :

$$\chi^{km} = \beta V^{km} - (\beta/2)(V^{kk} + V^{mm}) > 0, \quad k \neq m. \quad (2.6)$$

Here we use the energy unit to measure the absolute temperature so the Boltzmann constant is 1 and  $\beta$  is the inverse of the absolute temperature. We have assumed that all the three parameters are positive. This is because in a block copolymer, unlike monomers repel each other more than like ones do. We will see that in incompressible triblock copolymers these three parameters completely determine the interaction.

The Gibbs canonical distribution is

$$D(r) = \frac{1}{Z} \exp(-\beta H(r)), \quad Z = \int_\Gamma \exp(-\beta H(r)) d\mu \quad (2.7)$$

which describes the thermal equilibrium. The normalizing factor  $Z$  is called the partition function. The free energy of the system is  $-\beta^{-1} \log Z$ . If we define the microscopic density fields

$$\rho_k(x, r) := \sum_{i=1}^n \int_{i_k} \delta(x - r_i(\tau)) d\tau, \quad k = A, B, C, \quad (2.8)$$

then under this distribution the expectations

$$\langle \rho_k(x) \rangle := \int_\Gamma \rho_k(x, r) D(r) d\mu, \quad k = A, B, C \quad (2.9)$$

give the macroscopic densities of the  $A$ ,  $B$  and  $C$  monomers.

### 3 The self-consistent field theory

It is hopeless to find  $\langle \rho_k(x) \rangle$  directly from  $D$  due to the complexity of the interaction in  $H$ . However  $D$  satisfies a variational principle, whose proof may be found in many statistical mechanics text books (for instance [1], chapter 4).

**Proposition 3.1** For any other distribution  $D'$ ,

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

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

A distribution  $D'$  models a physical state, and  $S(D')$  is the entropy of this state, which is defined by  $-\int_{\Gamma} \log(D'(r)) D'(r) d\mu$ .

An approximation method comes to play based on this proposition. Consider a smaller class of distributions  $D'$ , and define

$$F(D') = \int_{\Gamma} H(r) D'(r) d\mu - \beta^{-1} S(D'). \quad (3.1)$$

$F(D')$  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 [9, 10, 11, 12, 14, 15] for different formulations), we choose the class of distributions to be those generated by a triple of external potential fields  $U = (U^A, U^B, U^C)$ , acting on the  $A$ ,  $B$  and  $C$  monomers respectively. It replaces the interaction between the monomers. We impose the restriction that for every  $x \notin \Omega$ ,  $U^k(x) = \infty$  ( $k = A, B, C$ ), to accommodate  $V_{\Omega}$ . We also assume that

$$\sum_k \frac{N_k}{N} \int_{\Omega} U^k(x) dx = 0. \quad (3.2)$$

The condition (3.2) 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. The Hamiltonian on  $\Gamma$  of such a system is

$$H_U(r) = \sum_i \sum_k \int_{i_k} U^k(r_i(\tau)) d\tau. \quad (3.3)$$

It induces a Gibbs canonical distribution

$$D_U(r) = \frac{1}{Z_U} \exp(-\beta H_U(r)), \quad Z_U = \int_{\Gamma} \exp(-\beta H_U(r)) d\mu. \quad (3.4)$$

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 approximate free energy under this  $U$  is

$$F(U) = \langle H \rangle_U - \beta^{-1} S(D_U). \quad (3.5)$$

Since (2.5) may be written in terms of  $\rho_k(x, r)$  as

$$H(r) = \int_{\Omega} \frac{V^{km}}{2\rho_0} \rho_k(x, r) \rho_m(x, r) dx, \quad (3.6)$$

the first term in (3.5), the average internal energy, is

$$\langle H \rangle_U := \int_{\Gamma} H(r) D_U(r) d\mu = \int_{\Omega} \frac{V^{km}}{2\rho_0} \langle \rho_k(x) \rangle_U \langle \rho_m(x) \rangle_U dx, \quad (3.7)$$

and the second term in (3.5) involves the entropy, which is calculated from the partition function  $Z_U$  [1],

$$\begin{aligned} S(D_U) &= \log Z_U - \beta \frac{\partial}{\partial \beta} \log Z_U \\ &= \log Z_U + \frac{\beta}{Z_U} \int_{\Gamma} \exp(-\beta H_U(r)) \left[ \sum_{i,k} \int_{i_k} U^k(r_i(\tau)) d\tau \right] d\mu \\ &= \log Z_U + \beta \int_{\Gamma} \left[ \sum_{i,k} \int_{i_k} U^k(r_i(\tau)) d\tau \right] D_U(r) d\mu \\ &= \log Z_U + \beta n \int_{\Gamma} \left[ \sum_k \int_{i_k} U^k(r_1(\tau)) d\tau \right] D_U(r) d\mu \\ &= \log Z_U + \beta \int_{\Omega} U^k(x) \langle \rho_k(x) \rangle_U dx. \end{aligned} \quad (3.8)$$

We now regard the approximate free energy  $F$  as a functional of the field  $U = (U^A, U^B, U^C)$ . Note that only  $\langle H \rangle_U$ , not  $S(D_U)$ , relates the effective field to the real interaction  $V$ .

The calculation of  $F(U)$  from  $U$  is done by the Feynman-Kac path integral theory (See [7], chapter 6). We note that because of the presence of  $V_{\Omega}$  that confines the molecules in  $\Omega$ ,  $U^k(x) = \infty$  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 theory. Let  $Q_U(y, \tau, z, t)$  be the fundamental solution of the backward equation

$$(Q_U)_{\tau} + (l^2/6)\Delta_y Q_U - \beta U Q_U = 0, \quad Q_U(y, t, z, t) = \delta(y - z), \quad (y, \tau) \in \Omega \times (0, t) \quad (3.9)$$

where  $U(y, \tau) = U^k(y)$  if  $\tau \in i_k$  ( $k = A, B, C$ ). Set  $q_U$  to be the solution of

$$(q_U)_{\tau} + (l^2/6)\Delta q_U - \beta U q_U = 0, \quad q_U(y, N) = 1, \quad (y, \tau) \in \Omega \times (0, N) \quad (3.10)$$

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

$$(q_U^*)_{\tau} - (l^2/6)\Delta q_U^* + \beta U q_U^* = 0, \quad q_U^*(y, 0) = 1, \quad (y, \tau) \in \Omega \times (0, N). \quad (3.11)$$

Note that

$$q_U(y, \tau) = \int_{\Omega} Q_U(y, \tau, z, N) dz, \quad q_U^*(y, \tau) = \int_{\Omega} Q_U(z, 0, y, \tau) dz. \quad (3.12)$$

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

$$\begin{aligned} Z_U &= \int_{\Gamma} \exp(-\beta H_U(r)) d\mu = \left\{ \int_{\Gamma_1} \exp(-\beta \sum_k \int_{i_k} U^k(r_1(\tau)) d\tau) d\mu_1 \right\}^n \\ &= \left\{ \int_{\Omega} [E_y \exp(-\beta \sum_k \int_{i_k} U^k(r_1(\tau)) d\tau)] dy \right\}^n \\ &= \left\{ \int_{\Omega} q_U(y, 0) dy \right\}^n = \left( \int_{\Omega} q_U^*(x, N) dx \right)^n. \end{aligned} \quad (3.13)$$

And the density  $\langle \rho_k(x) \rangle_U$  under  $U$

$$\begin{aligned}
\langle \rho_k(x) \rangle_U &= \frac{1}{Z_U} \int_{\Gamma} \left[ \sum_i \int_{i_k} \delta(r_i(\tau) - x) d\tau \right] \exp(-\beta H_U(r)) d\mu \\
&= \frac{n}{Z_U^{1/n}} \int_{\Gamma_1} \left[ \int_{i_k} \delta(r_1(\tau) - x) d\tau \right] \exp(-\beta \sum_k \int_{i_k} U^k(r_1(\tau)) d\tau) d\mu_1 \\
&= \frac{n}{Z_U^{1/n}} \int_{\Omega} \{ E_y \int_{i_k} \delta(r_1(\tau) - x) d\tau \exp(-\beta \int_0^N U(r_1(\tau), \tau) d\tau) \} dy \quad (3.14)
\end{aligned}$$

For any fixed  $\tau \in i_k$ ,

$$\begin{aligned}
&E_y \delta(r_1(\tau) - x) \exp(-\beta \int_0^N U(r_1(t), t) dt) \\
&= E_y \{ \delta(r_1(\tau) - x) \exp(-\beta \int_0^{\tau} U(r_1(t), t) dt) E_{r_1(\tau)}^{\tau} \exp(-\beta \int_{\tau}^N U(r_1(t), t) dt) \} \\
&= E_y \{ \delta(r_1(\tau) - x) \exp(-\beta \int_0^{\tau} U(r_1(t), t) dt) q_U(r_1(\tau), \tau) \} \\
&= q_U(x, \tau) E_y \delta(r_1(\tau) - x) \exp(-\beta \int_0^{\tau} U(r_1(t), t) dt) \\
&= q_U(x, \tau) Q_U(y, 0, x, \tau). \quad (3.15)
\end{aligned}$$

After integrating over  $y$  and  $\tau$  we obtain

$$\langle \rho_k(x) \rangle_U = \frac{n}{Z_U^{1/n}} \int_{i_k} q_U(x, \tau) q_U^*(x, \tau) d\tau. \quad (3.16)$$

This way  $Z_U$ ,  $\langle \rho_k(x) \rangle_U$ , and most importantly  $F(U)$  may be computed from (3.13) and (3.16).

## 4 Order parameters $\rho(x)$

In (3.5) the  $\langle H \rangle_U$  term, according to (3.7), depends on  $U$  through  $\langle \rho \rangle_U$ . We naturally take  $\langle \rho \rangle_U$  as order parameters, and invert (3.16) to express  $F$  in terms of  $\langle \rho \rangle_U$ . This idea was used in [16, 23] for diblock copolymers and in [20] for triblock copolymers.

To express the  $-\beta^{-1}S(D_U)$  term in  $F$  as a functional of  $\langle \rho \rangle_U$  we will take advantage of the fact that  $-S(D_U)$  as a functional of  $\langle \rho \rangle_U$  is the Legendre transform of  $-\log Z_U$  as a functional of  $\beta U$ . We start with calculating the derivative of  $-\log Z_U$  at  $\beta U$ . It is done by differentiating  $-\log Z_{U+\epsilon\phi}$  with respect to  $\epsilon$  where  $\phi = (\phi^A, \phi^B, \phi^C)$  is a variation of  $U$ . Defining  $\phi(y, t) = \phi^k(y)$  if  $\tau \in i_k$ , we set  $p = \frac{\partial q_{U+\epsilon\phi}}{\partial \epsilon} |_{\epsilon=0}$  and  $p^* = \frac{\partial q_{U+\epsilon\phi}^*}{\partial \epsilon} |_{\epsilon=0}$ . They are the solutions of

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

$$p_{\tau}^* - (l^2/6)\Delta p^* + \beta U p^* = -\beta \phi q_U^*, \quad p^*(x, 0) = 0 \quad (4.2)$$

which can be written as

$$p(x, \tau) = - \int_{\tau}^N \int_{\Omega} Q_U(x, \tau, y, t) q_U(y, t) \beta \phi(y, t) dy dt \quad (4.3)$$

$$p^*(x, \tau) = - \int_0^\tau \int_\Omega Q_U(y, t, x, \tau) q_U^*(y, t) \beta \phi(y, t) dy dt. \quad (4.4)$$

Then we deduce from (3.13) and (3.16)

$$\begin{aligned} \frac{d(-\log Z_{U+\epsilon\phi})}{d\epsilon} \Big|_{\epsilon=0} &= -\frac{n}{Z_U^{1/n}} \frac{\partial}{\partial \epsilon} \Big|_{\epsilon=0} \int_\Omega q_{U+\epsilon\phi}(y, 0) dy = -\frac{n}{Z_U^{1/n}} \int_\Omega p(y, 0) dy \\ &= \frac{n}{Z_U^{1/n}} \int_\Omega \int_0^N q_U(z, \tau) q_U^*(z, \tau) \beta \phi(z, \tau) d\tau dz \\ &= \int_\Omega \langle \rho_k(z) \rangle_U \beta \phi^k(z) dz. \end{aligned} \quad (4.5)$$

Hence

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

The equations (4.6) and (3.8) imply that  $-S(D_U)$  as a functional of  $\rho$  is the Legendre transform of  $-\log Z_U$  as a functional of  $\beta U$ . This is consistent with the conjugacy relation between  $\rho$  and  $\beta U$ . Consequently

$$\frac{\delta(-S(D_U))}{\delta(\langle \rho \rangle_U)} = -\beta U. \quad (4.7)$$

So if we can express  $\beta U$  in terms of  $\langle \rho \rangle_U$ , then by integrating  $\beta U$  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  $\beta U$ . Here we employ one of the several approximation steps in the paper. We linearize this dependence around  $\beta = 0$ , i.e.

$$\langle \rho_k(x) \rangle_U \approx \langle \rho_k(x) \rangle_0 + \frac{\partial \langle \rho_k(x) \rangle_{0+\epsilon U}}{\partial \epsilon} \Big|_{\epsilon=0}. \quad (4.8)$$

To justify this assumption we note that a copolymer melt exists in the room temperature above the freezing point. This linearization will lead to  $S(D_U)$  as a quadratic functional of  $\langle \rho \rangle_U$ . We compute from (3.16) as in (4.6),

$$\begin{aligned} &\frac{\partial \langle \rho_k(x) \rangle_{\epsilon U}}{\partial \epsilon} \Big|_{\epsilon=0} \\ &= -Z_0^{-\frac{1+n}{n}} \frac{\partial Z_{\epsilon U}}{\partial \epsilon} \Big|_{\epsilon=0} \int_{i_k} q_0(x, \tau) q_0^*(x, \tau) d\tau + \frac{n}{Z_0^{1/n}} \int_{i_k} (p(x, \tau) q_0^*(x, \tau) + p^*(x, \tau) q_0(x, \tau)) d\tau \\ &= \frac{\langle \rho_k(x) \rangle_0}{n} \int_\Omega \langle \rho_m(y) \rangle_0 \beta U^m(y) dy + \frac{n}{Z_0^{1/n}} \int_{i_k} (p(x, \tau) q_0^*(x, \tau) + p^*(x, \tau) q_0(x, \tau)) d\tau. \end{aligned} \quad (4.9)$$

Next we use another approximation: the thermodynamic limit of the system. We assume  $\Omega \rightarrow R^3$ , the entire space, and  $n \rightarrow \infty$  while keeping  $\frac{n}{|\Omega|} = \frac{\rho_0}{N}$  unchanged in the process. This approximation is justified by the fact that  $|\Omega|^{1/3} \gg l$ . Then we find

$$Q_0(y, \tau, z, N) \rightarrow \mathcal{K}(y-z, \tau-t) := \left( \frac{4\pi l^2 |\tau-t|}{6} \right)^{-3/2} \exp\left( -\frac{6(y-z)^2}{4l^2 |\tau-t|} \right), \quad (4.10)$$



where  $\mathcal{K}$  is the heat kernel in  $R^3$ . Consequently

$$q_0 \text{ and } q_0^* \rightarrow 1, \quad \frac{n}{Z_0^{1/n}} \rightarrow \frac{\rho_0}{N}, \quad \langle \rho_k(x) \rangle_0 \rightarrow \bar{\rho}_k := \frac{N_k \rho_0}{N}. \quad (4.11)$$

By (3.2) we deduce

$$\frac{\langle \rho_k(x) \rangle_0}{n} \int_{\Omega} \langle \rho_m(y) \rangle_0 \beta U^m(y) dy \rightarrow 0. \quad (4.12)$$

Moreover

$$p(x, \tau) \rightarrow - \int_{\tau}^N [\mathcal{K}(\cdot, \tau - t) * \beta U(\cdot, t)](x) dt, \quad p^*(x, \tau) \rightarrow - \int_0^{\tau} [\mathcal{K}(\cdot, \tau - t) * \beta U(\cdot, t)](x) dt. \quad (4.13)$$

Define

$$R_{km}(z) := \int_{i_k} \int_{i_m} \mathcal{K}(z, \tau - t) dt d\tau. \quad (4.14)$$

The linear approximation (4.8) becomes

$$\langle \rho_k \rangle_U \approx \bar{\rho}_k - \frac{\rho_0}{N} R_{km} * (\beta U^m). \quad (4.15)$$

Since the Fourier transform of  $\mathcal{K}$  is

$$\hat{\mathcal{K}}(\xi) := \int_{R^3} \mathcal{K}(x, t) e^{-2\pi i \xi \cdot x} dx = \exp\left(-\frac{4\pi^2 l^2 t \xi^2}{6}\right), \quad (4.16)$$

the Fourier transform of  $R_{km}$  in (4.14) is

$$\hat{R}_{km}(\xi) = \begin{cases} 2\left(\frac{2\pi l \xi}{\sqrt{6}}\right)^{-4} h\left(\frac{4\pi^2 l^2 \xi^2 N_k}{6}\right) & \text{if } k = m \\ \left(\frac{2\pi l \xi}{\sqrt{6}}\right)^{-4} g\left(\frac{4\pi^2 l^2 \xi^2 N_k}{6}, \frac{4\pi^2 l^2 \xi^2 N_m}{6}\right) & \text{if } k \neq m \end{cases} \quad (4.17)$$

where  $h(s) = e^{-s} + s - 1$ , and  $g(s, t) = (1 - e^{-s})(1 - e^{-t})$ .

Next we find an approximate inverse  $T$  of  $R$ , since the exact inverse is too complex. This is the third approximation we use in this section. Note the long and short wave expansions

$$h(s) \approx s, \quad g(s, t) \approx 1 \text{ if } s, t \gg 1 \quad (4.18)$$

$$h(s) \approx \frac{s^2}{2} - \frac{s^3}{6} + \frac{s^4}{24}, \quad g(s, t) \approx \left(s - \frac{s^2}{2} + \frac{s^3}{6}\right) \left(t - \frac{t^2}{2} + \frac{t^3}{6}\right) \text{ if } s, t \ll 1. \quad (4.19)$$

They lead to an approximate matrix of  $\hat{R}(\xi)$  whose inverse is

$$\hat{T}(\xi) = \frac{(2\pi l \xi)^2}{6N} K + \frac{6}{(2\pi l \xi)^2 N^3} L \quad (4.20)$$

where, with  $a = N_A/N$ ,  $b = N_B/N$ , and  $c = N_C/N$ ,

$$K = \frac{1}{2} \begin{bmatrix} \frac{1}{a} & 0 & 0 \\ 0 & \frac{1}{b} & 0 \\ 0 & 0 & \frac{1}{c} \end{bmatrix}, \quad L = \frac{3}{2(ab + bc + ca)} \begin{bmatrix} \frac{b+c}{a^2} & -\frac{c}{ab} & -\frac{b}{ca} \\ -\frac{c}{ab} & \frac{c+a}{b^2} & -\frac{a}{bc} \\ -\frac{b}{ca} & -\frac{a}{bc} & \frac{a+b}{c^2} \end{bmatrix}. \quad (4.21)$$

In [23] one may find a study for the accuracy of this approximation in the context of the diblock copolymer problem. Here the situation is similar. One may compare  $K$  and  $L$  here to  $A_S$  and  $A_L$  matrices in (2.21-2.24) of [20]. There the incompressibility condition (5.7) is imposed and one variable  $u_B$  is eliminated, so  $A_S$  and  $A_L$  are 2 by 2 matrices. After the inverse Fourier transform we find the operator

$$T = \frac{l^2}{6N}(-\Delta)K + \frac{6}{l^2N^3}(-\Delta)^{-1}L. \quad (4.22)$$

Here  $-\Delta$  comes from  $(2\pi\xi)^2$  and  $(-\Delta)^{-1}$  from  $1/(2\pi\xi)^2$ .

Now we reverse (4.15) to find  $\beta U$  expressed in terms of  $\langle \rho \rangle_U$ :

$$\beta U^k(x) \approx -\frac{N}{\rho_0} T^{km}(\rho_m - \bar{\rho}_m)(x). \quad (4.23)$$

In this context we simplify the notation  $\langle \rho \rangle_U$  to just  $\rho$ . So by integrating (4.23) we find

$$\begin{aligned} -S(D_U) + S(D_0) &\approx \frac{N}{2\rho_0} \int_{R^3} (T^{km}(\rho_k - \bar{\rho}_k))(\rho_m - \bar{\rho}_m) dx \\ &= \frac{1}{2\rho_0} \int_{R^3} \left[ \frac{l^2 K^{kk}}{6} |\nabla \rho_k|^2 + \frac{6L^{km}}{l^2 N^2} ((-\Delta)^{-1}(\rho_k - \bar{\rho}_k))(\rho_m - \bar{\rho}_m) \right] dx. \end{aligned} \quad (4.24)$$

In (4.24)  $(-\Delta)^{-1}(\rho_k - \bar{\rho}_k)$  may be written as an integral

$$(-\Delta)^{-1}(\rho_k - \bar{\rho}_k)(x) = \int_{R^3} \frac{\rho_k(y) - \bar{\rho}_k}{4\pi|x-y|} dy \quad (4.25)$$

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

Finally we return from the thermodynamic limit in  $R^3$  to the bounded domain  $\Omega$ . There are some choices of boundary conditions for  $(-\Delta)^{-1}$  on a bounded  $\Omega$ : The Dirichlet, the Neumann, and the periodic boundary conditions are the most obvious ones. They lead to different Green functions on  $\Omega$ . However the interior of the material is not significantly affected by the choice of the boundary condition. In [29] one may find a comparison between the Neumann and the periodic boundary conditions. Here we take the Neumann boundary condition as an example. Denote the Green function by  $G(x, y)$ . Then (4.24) becomes

$$-S(D_U) + S(D_0) \approx \frac{1}{2\rho_0} \int_{\Omega} \left[ \frac{l^2 K^{kk}}{6} |\nabla \rho_k(x)|^2 + \frac{6L^{km}}{l^2 N^2} \left( \int_{\Omega} G(x, y)(\rho_k(y) - \bar{\rho}_k) dy \right) (\rho_m(x) - \bar{\rho}_m) \right] dx. \quad (4.26)$$

A more elegant way to express the above expression is to introduce the nonlocal operator  $(-\Delta)^{-1/2}$ , the square root of the inverse of

$$-\Delta : \{\eta \in W^{2,2}(\Omega) : \partial_\nu \eta = 0 \text{ on } \partial\Omega, \bar{\eta} = 0\} \rightarrow \{\theta \in L^2(\Omega) : \bar{\theta} = 0\}. \quad (4.27)$$

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

$$\int_{\Omega} \left[ \int_{\Omega} G(x, y)(\rho_k(y) - \bar{\rho}_k) dy (\rho_m(x) - \bar{\rho}_m) \right] dx = \int_{\Omega} ((-\Delta)^{-1/2}(\rho_k - \bar{\rho}_k))((-\Delta)^{-1/2}(\rho_m - \bar{\rho}_m)) dx. \quad (4.28)$$

As we combine the entropy and (3.7) to form  $F$  as a functional of  $\rho$  from (3.5), we drop the unimportant constant  $S(D_0)$ :

$$F(\rho) = \int_{\Omega} \left[ \frac{l^2 K^{kk}}{12\beta\rho_0} |\nabla \rho_k|^2 + \frac{3L^{km}}{l^2 N^2 \beta \rho_0} ((-\Delta)^{-\frac{1}{2}}(\rho_k - \bar{\rho}_k))((-\Delta)^{-\frac{1}{2}}(\rho_m - \bar{\rho}_m)) + \frac{V^{km}}{2\rho_0} \rho_k \rho_m \right] dx. \quad (4.29)$$

## 5 The incompressibility condition

To separate the size effect of  $\Omega$  from the shape effect of  $\Omega$ , we scale  $\Omega$  to  $D = \{x : |\Omega|^{1/3}x \in \Omega\}$ , whose 3-dimensional Lebesgue measure is 1. In this section we assume that  $D$  is fixed but  $|\Omega|^{1/3}$  may vary. In the mean time introduce relative densities  $u_k(x) = \rho_k(|\Omega|^{1/3}x)/\rho_0$ , and let  $u = (u_A, u_B, u_C)^T$  and  $\bar{u} = (\bar{u}_A, \bar{u}_B, \bar{u}_C)^T$ , where  $\bar{u}_k := \int_D u_k(x) dx$  denotes the average of  $u_k$ . Hereinafter the superscript  $T$  denotes the transpose operation on a vector. The relative densities turn (4.29) to a dimensionless form for  $I = \beta F/(\rho_0|\Omega|)$ , the relative free energy per monomer,

$$I(u) = \int_D \left[ \frac{1}{2} \epsilon^2 \nabla u \cdot \nabla u + \frac{1}{2} \sigma ((-\Delta)^{-\frac{1}{2}}(u - \bar{u})) \cdot ((-\Delta)^{-\frac{1}{2}}(u - \bar{u})) + W(u) \right] dx. \quad (5.1)$$

The coefficients  $\epsilon^2$  is a diagonal matrix, where  $\epsilon^2$  is written as a square for reasons beyond this paper (see [29, 26] where  $\epsilon$  is proportional to the thickness of interfaces between microdomains), and  $\sigma$  is a symmetric matrix. They are derived from  $K$  and  $L$  in (4.21):

$$(\epsilon^2)^k := (\epsilon^2)^{kk} = \frac{l^2}{6|\Omega|^{2/3}} K^{kk}, \quad \sigma^{km} = \frac{6|\Omega|^{2/3}}{l^2 N^2} L^{km}. \quad (5.2)$$

The first and second terms in (5.1) are written in matrix forms, i.e.

$$\epsilon^2 \nabla u \cdot \nabla u = (\epsilon^2)^k |\nabla u_k|^2, \quad (5.3)$$

$$\sigma (-\Delta)^{-\frac{1}{2}}(u - \bar{u}) \cdot (-\Delta)^{-\frac{1}{2}}(u - \bar{u}) = \sigma^{km} (-\Delta)^{-\frac{1}{2}}(u_k - \bar{u}_k) (-\Delta)^{-\frac{1}{2}}(u_m - \bar{u}_m). \quad (5.4)$$

The third integrand comes from the internal energy (3.7):

$$W(u) = \frac{\beta V^{km}}{2} u_k u_m. \quad (5.5)$$

Since the total number of  $A$  ( $B$  and  $C$  respectively) monomers in  $\Omega$  is  $nN_A = nNa$  ( $nNb$  and  $nNc$  respectively), we have the monomer number constraints

$$\bar{u}_A = a, \quad \bar{u}_B = b, \quad \bar{u}_C = c, \quad (5.6)$$

where  $a + b + c = 1$ .

Now we assume that the copolymer is incompressible, i.e.

$$u_A(x) + u_B(x) + u_C(x) = 1, \quad \forall x \in D. \quad (5.7)$$

Under this constraint the  $W$  term in (5.1) satisfies

$$W(u) = \begin{cases} (\beta V^{km}/2) u_k u_m & \text{if } u_A + u_B + u_C = 1, \quad 0 \leq u_A, u_B, u_C \leq 1 \\ \infty & \text{otherwise} \end{cases}. \quad (5.8)$$

They ensure that on  $0 \leq u_k \leq 1$  and  $u_A + u_B + u_C = 1$ ,  $W$  is typically concave and there exist three local minima at  $(1, 0, 0)$ ,  $(0, 1, 0)$  and  $(0, 0, 1)$ . To make (5.8) more mathematically tractable, we may change  $W$  to a smooth function defined on  $R^3$ , while retaining its basic properties. Moreover if  $W$  is chosen in such a way, the incompressibility condition (5.7) may be dropped and we may study compressible triblock copolymers.

The Euler-Lagrange equation of (5.1) may be written as an elliptic system:

$$\begin{cases} -\epsilon^2 \Delta u + \sigma v + W'(u) = \eta \\ -\Delta v = u - \bar{u} \\ \partial_\nu u = \partial_\nu v = 0 \text{ on } \partial D \\ \bar{u} = (a, b, c)^T, \bar{v} = (0, 0, 0)^T \end{cases}. \quad (5.9)$$

Here  $W'$  denotes the gradient of  $W$ .  $\eta$  in the first equation is a vector of three Lagrange multipliers corresponding to the constraint  $\bar{u} = (a, b, c)^T$ . (5.9) is written for the case of compressible block copolymers. If the incompressibility condition is assumed, we add one unknown function  $\xi(x)$  to each component of  $\eta$  to accommodate the constraint (5.7).

The functional  $I$ , defined in (5.1), is minimized in the admissible set

$$X = \{(u_A, u_B, u_C)^T : u_A, u_B, u_C \in W^{1,2}(D) \text{ satisfy (5.6), (5.7)}\}. \quad (5.10)$$

In the case of a compressible copolymer melt (5.7) is dropped in the definition of  $X$  provided that  $W$  has the triple well shape. Also there is no boundary condition on  $u$  in  $X$ . Any critical point of  $I$  will satisfy the Neumann boundary condition. The tangent space of  $X$  is

$$T = \{(\psi_A, \psi_B, \psi_C)^T : \psi_k \in W^{1,2}(D), \bar{\psi}_k = 0 \forall k, \sum_k \psi_k = 0\}. \quad (5.11)$$

The first and second derivatives of  $I$  are, for  $u \in X$  and  $\psi, \zeta \in T$ ,

$$I'(u)\psi = \int_D [\epsilon^2 \nabla u \cdot \nabla \psi + \sigma (-\Delta)^{-\frac{1}{2}} u \cdot (-\Delta)^{-\frac{1}{2}} \psi + W'(u) \cdot \psi] dx, \quad (5.12)$$

$$I''(u)(\psi, \zeta) = \int_D [\epsilon^2 \nabla \psi \cdot \nabla \zeta + \sigma (-\Delta)^{-\frac{1}{2}} \psi \cdot (-\Delta)^{-\frac{1}{2}} \zeta + W''(u)\psi \cdot \zeta] dx, \quad (5.13)$$

where  $W''$  is the hessian of  $W$ .

## 6 Disordered phase and weak segregation

A critical point of  $I$  is a  $u \in X$  such that  $I'(u)\psi = 0$  for all  $\psi \in T$ .  $u = (a, b, c)$  is the only constant critical point. When it is stable, i.e. it is a local minimum of  $I$ , the copolymer is in the disordered phase with homogeneous monomer densities. To understand the stability of  $(a, b, c)$ , let us start with the eigenvalues and eigenfunctions  $(\lambda_j, f_j)$ ,  $j = 1, 2, \dots$ , of  $-\Delta$  on  $D$  under the Neumann boundary condition, i.e.

$$-\Delta f_j = \lambda_j f_j \text{ in } D, \partial_\nu f_j = 0 \text{ on } \partial D, \|f_j\|_2 = 1, \bar{f}_j = 0, \lambda_j > 0, \quad (6.1)$$

excluding the first eigenvalue  $\lambda_0 = 0$  since the corresponding eigenfunction has nonzero average. An example is  $D = (0, d_1) \times (0, d_2) \times (0, d_3)$ ,  $d_1 d_2 d_3 = 1$ , and the eigenfunctions and eigenvalues are

$$f_j(x) = \sqrt{8} \prod_{i=1}^3 \cos \frac{j_i \pi x_i}{d_i}, \quad \lambda_j = \sum_{i=1}^3 \left( \frac{j_i \pi}{d_i} \right)^2 \quad (6.2)$$

where  $j_1, j_2, j_3$  range over  $0, 1, 2, \dots$  but  $j_1^2 + j_2^2 + j_3^2 \neq 0$ . We perturb  $(a, b, c)$  by  $\psi \in T$  and expand  $\psi$  under these eigenfunctions:

$$\psi = \sum_{j=1}^{\infty} f_j e_j, \quad e_j \in E = \{(h_A, h_B, h_C)^T \in R^3 : h_A + h_B + h_C = 0\}, \quad (6.3)$$

where  $E$  is a 2-dimensional linear subspace of  $R^3$ . The second derivative of  $I$  at  $(a, b, c)$  along  $(\psi, \psi)$  may be written in terms of  $e_j$ :

$$\begin{aligned} I''(a, b, c)(\psi, \psi) &= \sum_{j=1}^{\infty} (\lambda_j \epsilon^2 e_j \cdot e_j + \frac{1}{\lambda_j} \sigma e_j \cdot e_j + \beta V e_j \cdot e_j) \\ &= \sum_{j=1}^{\infty} (\lambda_j \epsilon_E^2 e_j \cdot e_j + \frac{1}{\lambda_j} \sigma_E e_j \cdot e_j + \beta V_E e_j \cdot e_j). \end{aligned} \quad (6.4)$$

Here we have introduced linear operators  $\epsilon_E^2$ ,  $\sigma_E$ , and  $\beta V_E : E \rightarrow E$ , which are derived from  $\epsilon^2$ ,  $\sigma$ , and  $\beta V$  respectively. If we let  $I_E : E \rightarrow R^3$  be the inclusion and  $P_E : R^3 \rightarrow E$  the projection,

$$\epsilon_E^2 = P_E \epsilon^2 I_E, \quad \sigma_E = P_E \sigma I_E, \quad \beta V_E = \beta P_E V I_E. \quad (6.5)$$

If  $b_1$  and  $b_2$  form a basis in  $E$ , the operators are represented by the matrices

$$\epsilon_E^2 = \begin{bmatrix} b_1^T \epsilon^2 b_1 & b_1^T \epsilon^2 b_2 \\ b_2^T \epsilon^2 b_1 & b_2^T \epsilon^2 b_2 \end{bmatrix}, \quad \sigma_E = \begin{bmatrix} b_1^T \sigma b_1 & b_1^T \sigma b_2 \\ b_2^T \sigma b_1 & b_2^T \sigma b_2 \end{bmatrix}, \quad V_E = \begin{bmatrix} b_1^T V b_1 & b_1^T V b_2 \\ b_2^T V b_1 & b_2^T V b_2 \end{bmatrix}. \quad (6.6)$$

To determine the positivity of these matrices let us temporarily choose  $b_1 = (1, -1, 0)^T$  and  $b_2 = (1, 0, -1)^T$ . Under this basis we find from (4.21) and (2.6)

$$\epsilon_E^2 = \frac{l^2}{12|\Omega|^{2/3}} \begin{bmatrix} \frac{1}{a} + \frac{1}{b} & \frac{1}{c} \\ \frac{1}{c} & \frac{1}{a} + \frac{1}{b} \end{bmatrix}, \quad (6.7)$$

$$\sigma_E = \frac{9|\Omega|^{2/3}}{l^2 N^2 (ab + bc + ca)} \begin{bmatrix} \frac{b+c}{a^2} + \frac{c+a}{b^2} + \frac{2c}{ab} & \frac{b+c}{a^2} + \frac{c}{ab} + \frac{b}{ca} - \frac{a}{bc} \\ \frac{b+c}{a^2} + \frac{c}{ab} + \frac{b}{ca} - \frac{a}{bc} & \frac{b+c}{a^2} + \frac{a+b}{c^2} + \frac{2b}{ca} \end{bmatrix}, \quad (6.8)$$

$$\beta V_E = \begin{bmatrix} -2\chi^{AB} & -\chi^{AB} - \chi^{CA} + \chi^{BC} \\ -\chi^{AB} - \chi^{CA} + \chi^{BC} & -2\chi^{CA} \end{bmatrix}. \quad (6.9)$$

$\epsilon_E^2$  is clearly positive definite.  $\sigma_E$  is also positive since its determinant is

$$\frac{81|\Omega|^{4/3}(a+b+c)^2}{l^4 N^4 (ab+bc+ca)a^2 b^2 c^2} > 0. \quad (6.10)$$

About  $\beta V_E$  we note that remarkably it depends on the Flory-Huggins parameters only. This verifies the point that we raised in Section 2.  $\beta V_E$  has at least one negative eigenvalue, but since its determinant is

$$2\chi^{AB}\chi^{BC} + 2\chi^{BC}\chi^{CA} + 2\chi^{CA}\chi^{AB} - (\chi^{AB})^2 - (\chi^{BC})^2 - (\chi^{CA})^2 \quad (6.11)$$

which may be any real number depending on  $\chi^{AB}$ ,  $\chi^{BC}$  and  $\chi^{CA}$ , the matrix may be negative definite, indefinite or degenerate. A stability criterion is formulated based on (6.4).

**Proposition 6.1** *The critical point  $(a, b, c)$  of  $I$  is stable if the linear operator  $\lambda_j \epsilon_E^2 + \frac{1}{\lambda_j} \sigma_E + \beta V_E$  on  $E$  is positive definite for all the positive eigenvalues  $\lambda_j$  of  $-\Delta$  on  $D$ .*

Because the positive matrix  $\lambda_j \epsilon_E^2$  dominates  $\lambda_j \epsilon_E^2 + \frac{1}{\lambda_j} \sigma_E + \beta V_E$  when  $\lambda_j$  is large, we only need to test its positivity for finitely many  $\lambda_j$ . In particular the criterion holds if all  $\chi^{km} N$  are small. The smallness here is measured against  $a$ ,  $b$ , and  $c$  only. The parameters  $l$  and  $|\Omega|$  in  $\epsilon_E^2$  and  $\sigma_E$  cancel out. Moreover if  $\lambda \epsilon_E^2 + \frac{1}{\lambda} \sigma_E + \beta V_E$  is positive for all positive  $\lambda$ ,  $(a, b, c)$  becomes stable independent of  $D$ . In this case since  $\epsilon_E^2$  and  $\sigma_E$  are both positive definite, one need only to consider  $\lambda$  in a compact subset of  $(0, \infty)$ . An instability result is also available following (6.4).

**Proposition 6.2** *If the linear operator  $\lambda_j \epsilon_E^2 + \frac{1}{\lambda_j} \sigma_E + \beta V_E$  on  $E$  has a negative eigenvalue at an eigenvalue  $\lambda_j$  of  $-\Delta$  on  $D$ ,  $(a, b, c)$  is unstable.*

The phenomenon of weak segregation occurs when  $\lambda_j \epsilon_E^2 + \frac{1}{\lambda_j} \sigma_E + \beta V_E$  fails to be positive definite at some  $\lambda_j$ . Such a  $\lambda_j$  gives rise to an unstable perturbation  $\psi = f_j e_j$  where  $e_j$  is an eigenvector corresponding to a negative eigenvalue of the matrix. In the copolymer the monomer densities develop inhomogeneity along such a mode. This is also known as spinodal decomposition. It signals the beginning of the micro-domain separation process. The domains where one type of the  $A$ ,  $B$  and  $C$  monomers are rich are still small, and the interfaces between them are not yet sharp, simply because  $f_j$  has no sharp internal or boundary layers. Later due to nonlinear effects, the domains will grow into larger size and the interfaces become sharp layers, a phenomenon known as strong segregation, which is studied in [29].

To illustrate the weak segregation in more detail we consider the very special case  $a = b = c = \frac{1}{3}$  and  $\chi := \chi^{AB} = \chi^{BC} = \chi^{CA}$ . Under the orthonormal basis  $b_1 = \frac{1}{\sqrt{6}}(2, -1, -1)^T$  and  $b_2 = \frac{1}{\sqrt{2}}(0, -1, 1)^T$ , with the identity matrix in  $E$  denoted by  $1_E$ , we obtain

$$\epsilon_E^2 = \frac{l^2}{6|\Omega|^{2/3}} \frac{3}{2} 1_E, \quad \sigma_E = \frac{6|\Omega|^{2/3}}{l^2 N^2} \frac{3^4}{2} 1_E, \quad \beta V_E = -\chi 1_E. \quad (6.12)$$

According to Propositions 6.1 and 6.2,

$$\lambda \epsilon_E^2 + \frac{1}{\lambda} \sigma_E + \beta V_E = \left( \frac{l^2}{6|\Omega|^{2/3}} \frac{3}{2} \lambda + \frac{6|\Omega|^{2/3}}{l^2 N^2} \frac{3^4}{2} \frac{1}{\lambda} - \chi \right) 1_E \quad (6.13)$$

is positive definite for all positive  $\lambda$  exactly when  $\chi N < 9\sqrt{3}$ , in which case  $(a, b, c)$  is stable. If  $\chi N > 9\sqrt{3}$ , the most unstable modes are found around  $\lambda_j \approx 18\sqrt{3}|\Omega|^{2/3}/(l^2 N)$  when the first two terms on the right side of the last equation are equal. The eigenfunctions  $f_j$  corresponding to these  $\lambda_j$  show how monomer density inhomogeneity is developed. In the case  $D = (0, 1) \times (0, 1) \times (0, 1)$ ,

the eigenfunctions are given in (6.2) with  $(j_1\pi)^2 + (j_2\pi)^2 + (j_3\pi)^2 = \lambda_j$ . This determines  $j_1$ ,  $j_2$  and  $j_3$ . The size of microdomains in this early separation stage is  $(1/j_1) \times (1/j_2) \times (1/j_3)$  in  $D$ , which corresponds to  $s_1 \times s_2 \times s_3$  in the real domain  $\Omega$  with

$$s_1 = \frac{|\Omega|^{1/3}}{j_1}, \quad s_2 = \frac{|\Omega|^{1/3}}{j_2}, \quad s_3 = \frac{|\Omega|^{1/3}}{j_3}. \quad (6.14)$$

Our analysis has shown that

$$\frac{1}{s_1^2} + \frac{1}{s_2^2} + \frac{1}{s_3^2} \approx \frac{18\sqrt{3}}{\pi^2 l^2 N}. \quad (6.15)$$

So the smallest of  $s_1$ ,  $s_2$  and  $s_3$  is of the order  $\sqrt{N}l$ .

## 7 Discussion

We believe that (5.1) should at least qualitatively describe the phenomena of weak and strong segregation in triblock copolymers. Several morphology phases such as the lamellar phase, which is rigorously studied in [29], and the core-shell phase [2] may also be modeled by (5.1).

The order/disorder phase transition point  $9\sqrt{3}$  for  $\chi N$  when  $a = b = c$  and  $\chi := \chi^{AB} = \chi^{BC} = \chi^{CA}$  derived in Section 6 should be checked experimentally. The following approximation steps used in this paper may cause inaccuracy.

The self-consistent field theory is generally considered to work well for high molecular weight polymers. The linearization (4.8) of (3.16) becomes inaccurate if  $\beta$  is too large, i.e. the temperature is too low. This may be improved by adding higher order expansion terms in (4.15). The approximation of  $\Omega$  by  $R^3$  in finding  $T$  in Section 4 only affects the model near the boundary of  $\Omega$ , which is not of too much importance. This inconsistency is reflected in the change from the Dirichlet boundary condition satisfied by  $\langle \rho(x) \rangle_U$  under every  $U$  in Section 3 to the Neumann boundary condition satisfied by any critical point  $u$  of  $I$  in Section 5.

When  $\hat{T}$  is computed, a crucial long,  $\xi^2$ , and short,  $\xi^{-2}$ , wave approximation is used. This eventually leads to the  $\epsilon^2$  and the  $\sigma$  terms in (5.1). More terms of other orders of  $\xi$  may be added, at the expense of having extra nonlocal integrands in (5.1), which are more complex than the  $\sigma$  term.

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