FIELD-INDUCED PHASE TRANSITIONS OF BLOCK COPOLYMERS

Field-induced Phase Transitions of Block Copolymers

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Abstract

Block copolymers are a class of soft materials which can self-assemble into a variety of ordered structures. One method to induce new structures is the application of an external field such as an electric field. Previously, studies of the field-induced phase transitions are based on the assumption that the structural change follows certain symmetry pattern or simply using real-space numerical methods. The goal of the current project is to develop a simple analytic method to predict the structural change. Our approach is based on a linear response theory, in which the external field is taken as a perturbation and the lowest-order contribution to the solution is computed. We applied our method to the Landau-Brazovskii theory which is valid close to the order-disorder transition point of diblock copolymers. The result shows that there will be an additional term to the order parameter as a response to the external field. The structural change can be predicted by a new Fourier expansion of the order parameter. As an example, we examined the structural change of a body-centered cubic phase under an applied electric field.

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f	volume fraction of monomer A in a diblock copolymer
χ	Flory-Huggins segment-segment interaction parameter
N	degree of polymerization
N_A	number of A-monomer in a diblock copolymer
F_b	bulk diblock copolymer free energy per polymer chain
F_{es}	electrostatic energy contribution per polymer chain
F_{tot}	total free energy per polymer chain
Ω	system volume
ν_p	volume per chain segment
R_g	radius of gyration
b	Kuhn length
ξ_0	bare correlation length
q_0	critical wave vector
τ_0	reduced tempertaure
γ_0, λ_0, λ, u	expansion coefficients determined by f
ξ, τ, γ	scaled coefficients of ξ_0, τ_0 and γ_0
$\kappa(\vec{r})$, $\kappa(\mathbf{r})$	local dielectric constant
κ_A, κ_B	dielectric constant of monomer A and monomer B
ϕ, $\phi(\vec{r})$	order parameter (density profile in the block copolymer case)

$\psi(\vec{r})$, $\psi(\mathbf{r})$	local electrostatic potential
μ	Lagrange multiplier

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Chapter 1

Introduction

Block copolymers are macromolecules made by joining two or more chemically distinct polymer blocks. Each polymer block is a sequence of identical monomers [1]. There are almost unlimited numbers of molecular configurations for block copolymers as we can change the number of chemically distinct blocks and the ways they are linked into a block copolymer (linear versus branched sequencing). A small subset of possible molecular architectures for bock copolymers is illustrated in Figure 1.1, presenting several commonly encountered types of combinations. The simplest architecture is the linear AB diblock copolymer, which is made of two polymers A and B covalently bonded together. Driven by the chemical incompatibilities between the different blocks, block copolymers tend to phase separate under certain temperatures. Due to the covalent bonds between blocks in block copolymers, they can not phase separate at a macroscopic length scale. Instead, they go through mesoscopic self-assembly leading to ordered microphases. Figure 1.2 shows three representative diblock phases [1].

There are several factors controlling the phase behavior of diblock polymers. One is the composition f, which is defined as the volume fraction of A-monomer in a

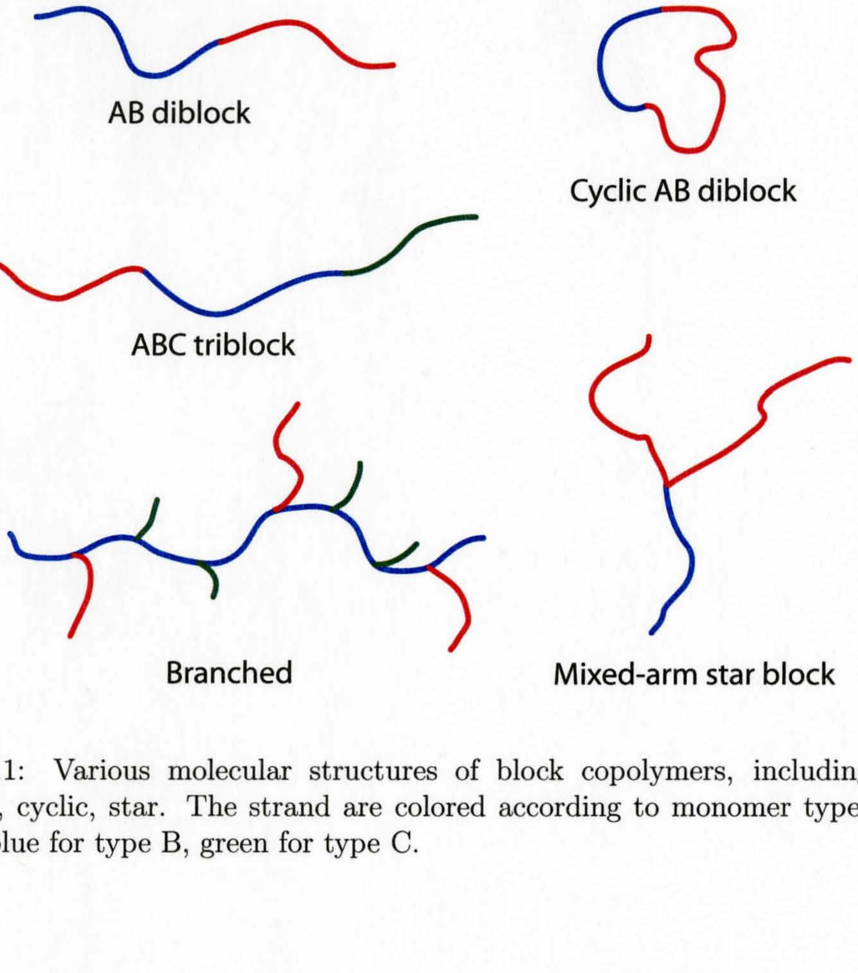
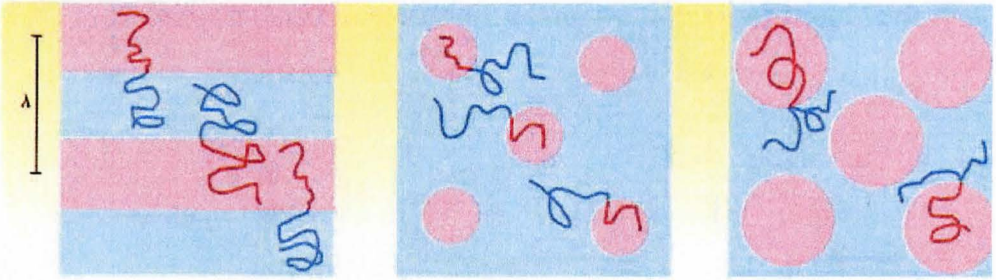


Figure 1.1: Various molecular structures of block copolymers, including linear, branched, cyclic, star. The strand are colored according to monomer type, red for type A, blue for type B, green for type C.



$f_A=1/2$ AB linear

$f_A>1/2$ AB linear

$f_A=1/2$ A_2B branched

Figure 1.2: Possible morphologies of block copolymers. Symmetric linear AB diblocks can form lamellar structure. A cylindrical or spherical morphology can be formed when the volume fraction of one block is increased. Branched A_2B diblocks with equal volume fraction for A and B can result in a nonlamellar morphology. (Adopted from [1]).

polymer chain $f = \frac{N_A}{N}$. As illustrated in Figure 2a and 2b, lamellar phase changes to a cylindrical or spherical structure as the volume fraction of A block is increased. Another factor is the Flory-Huggins segment-segment interaction parameter χ [2], [3],

$$\chi = \frac{1}{k_BT}[\epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{AB})], \tag{1.1}$$

where ϵ_{ij} is the contact energy between the i segment and the j segment. The parameter χ describes the cost of free energy , in units of the thermal energy, for A-B monomers in contact. It varies inversely with temperature. The product of this parameter and N (degree of polymerization) controls the state of segregation [1].

Self-consistent field theory is one of the most accurate theories for the study of block-copolymer phase behaviors. Helfand and his coworkers developed this self-consistent field theory (SCFT) in mid-1970's [4]. The essential part of SCFT is evaluating the exact equilibrium behavior of a single block copolymer subjected to the mean field derived self-consistently from the density. Later, Leibler predicted the phase behavior in the weak segregation limit where the interactions between the different polymers are weak. He used the so-called WSL theories [5], which are valid near the order-disorder transition (ODT). In general, the free energy is written as a functional of the Fourier transform of the concentration profile. The strong segregation theories developed by Semenov are successful at predicting phase behavior far away form the ODT [6]. In this region, the chains are strongly stretched, the interface where the A and B segments contact each other is very narrow. In this case, the interaction and stretching energies can be treated separately and the free energy is given in a simple form. Besides these approximate theories, the SCFT can be solved exactly using numerical methods [7], [8]. Figure 1.3 illustrated the phase diagram calculated by Masten for an AB diblock copolymer using SCFT theory [8]. The phase diagram is symmetric about $f = 0.5$ and shows five ordered morphologies: spherical (S), cylindrical (C), gyroid (G) lamellar (L) and spheres on a close-packed

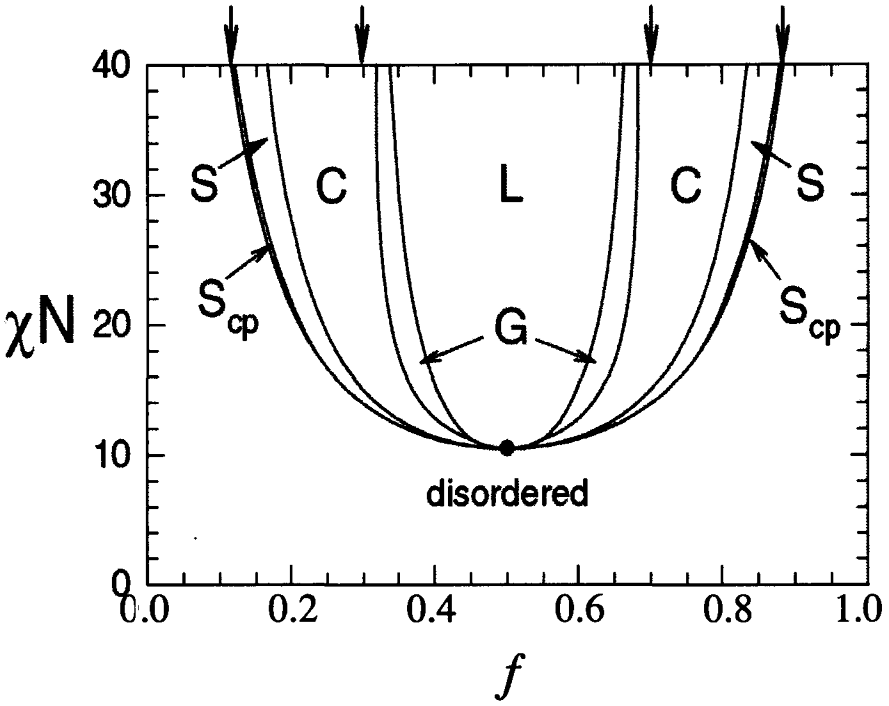


Figure 1.3: Phase diagram calculated using SCFT. From inside out, the phases are: lamellar (L), gyroid (G), cylindrical (C), Spherical (S). (Adopted from [8]).

lattice (S_{cp}). Different phases occur at different values of the composition f and the parameter χN. For $\chi N < 10.5$, a homogeneous disordered phase is predicted. At larger values of χN, nearly symmetric diblocks form a lamellar phase. Diblocks with intermediate levels of compositional asymmetry form a hexagonally packed cylindrical phase. A complex gyroid phase occurs in a narrow region between the lamellar and cylindrical phase when the levels of compositional asymmetry for diblocks are between the previous two. This gyroid phase is a three-dimensional bicontinuous structure [9]. At much higher compositional asymmetry, a body-centered cubic spherical phase is found to be the stable one. This phase diagram from the SCFT theory turns out to have overall agreement with experiment results.

The Laudau-Brazovskii theory of weak crystallization is a simply theory developed by Brazovakii in 1975. This theory can be applied to diblock copolymers [10], [11]. In this theory, the free energy is given as a functional of the density profile to the fourth order. This theory is general for systems that undergo a phase transition between the disordered liquid and ordered crystalline phases driven by a short-wavelength instability. It can be applied to diblock copolymers. In the mean-field approximation, this theory can account for all the ordered phases of diblock copolymers [12]. It can be cast in the reciprocal space to obtain the ordered structures. In principle there are infinite sets of reciprocal lattice vectors for the density function. The set of shortest reciprocal lattice vectors corresponds to the fundamental harmonic of the density [12]. The one mode approximation includes only the shortest wave vectors, and is a good approximation for weakly-interacting systems.

As mentioned above, block copolymers can self-assemble into a wide variety of ordered arrays with a characteristic size determined by the chain size. This feature attracts people to study the application of these ordered structures on nanotechnology. Examples are high density porous materials and fabrication of nanoscopic device [13],

[14]. However, in general the ordered phase is not created as perfect single crystals, but rather it is formed by domains of different orientations. Lack of long-range order is one of the sources delaying the application of these materials. To be useful, these domains need to be oriented. Control over the microdomain alignment can be achieved by applying a symmetry breaking field.

Electric fields have been shown to be an effective method of controlling microdomain orientation [15], [16], [17]. Due to the difference in dielectric constants of the microdomains, orientation-dependent polarization will occur when an electric field is applied. The electrostatic forces exerted onto the dielectric interface can be minimized when the dielectric interfaces are aligned parallel to the electric field. Experimental studies and theoretical calculations show that electric fields can align the microdomains in the direction of the applied field to lower the free energy, as well as induce phase transitions [18]. It is known that electric fields can align the lamellar and cylindrical microdomains of diblock copolymers both in bulk and in thin films [19], [20]. Studies showed how a block-copolymer films with cylindrical domains oriented vertical to the surface are created by applying a strong perpendicular electric field. In a monolayer of spherical domains, a strong electric field perpendicular to the surface of the monolayer causes the sphere to elongate in the direction of the field and finally transform into cylinders parallel to the electric vector [21]. In films with multiple layers of spheres, the spherical microdomains can deform into ellipsoids when an electric filed is applid, and under sufficiently high electric fields the ellipsoids can further stretch to a level that they interconnect to form cylinders [22]. Studies also showed that well-ordered pattern on the micron size scale can be generated by applying electric field on diblock copolymer films as the field enhances the fluctuations on a polymer surface [23]. The long-rang ordered block copolymers formed by applying the electric field turns out to have many application. For instance, perpendicular cylindrical domains are used in the construction of nanoporous membrancs. There is also theoretical work showing how a strong electric field can effect the stability of a lamellar layer of diblock copolymer [24].

Several theoretical works have been carried out on the study of electric field induced phase transitions. One problem of interest is how the body-centered-cubic (BCC) phase changes under electric field. Unlike lamellar and cylindrical phases in which the free energy penalty associated with dielectric interfaces can be eliminated by reorientation, BCC spheres can only distort to reduce free energy. The deformation of BCC phase has been examined by SCFT which is valid at any polymer segregation [18]. Assuming that the phase transition occurs along a specific pathway, Lin et al have solved the SCFT in the presence of a applied electric field along (1, 1, 1) direction. They assumed that the BCC structure changes to an ordered array of ellipsoids with a $R\bar{3}m$ symmetry, and showed that the ellipsoids transform to a cylindric phase at strong electric fields. The SCFT used in the study for the structure change of BCC phase under electric field shows that when there are presence of dissociated ions in block copolymers phase transition occurs at a much smaller electric field [25]. The SCFT equations with an applied electric field can also be solved in real-space using numerical methods. Recently Jiang et al have carried out real-space calculations for electric fields along different directions. Some results from their studies are shown in Figure 1.4 [26]. The pictures in the left column are the starting state. Electric fields are applied along the (0, 1, 0), (1, 1, 0) and (1, 1, 1) directions from top to bottom, respectively. For all the three cases, spheres are elongated along the direction of the electric field. The elongated spheres ultimately interconnect to cylinders with the long axis in the direction of the electric field.

A relatively simple theoretical study is based on the single-mode approximation [27]. This approach uses the Ginzburg-Landau like free energy and includes the full

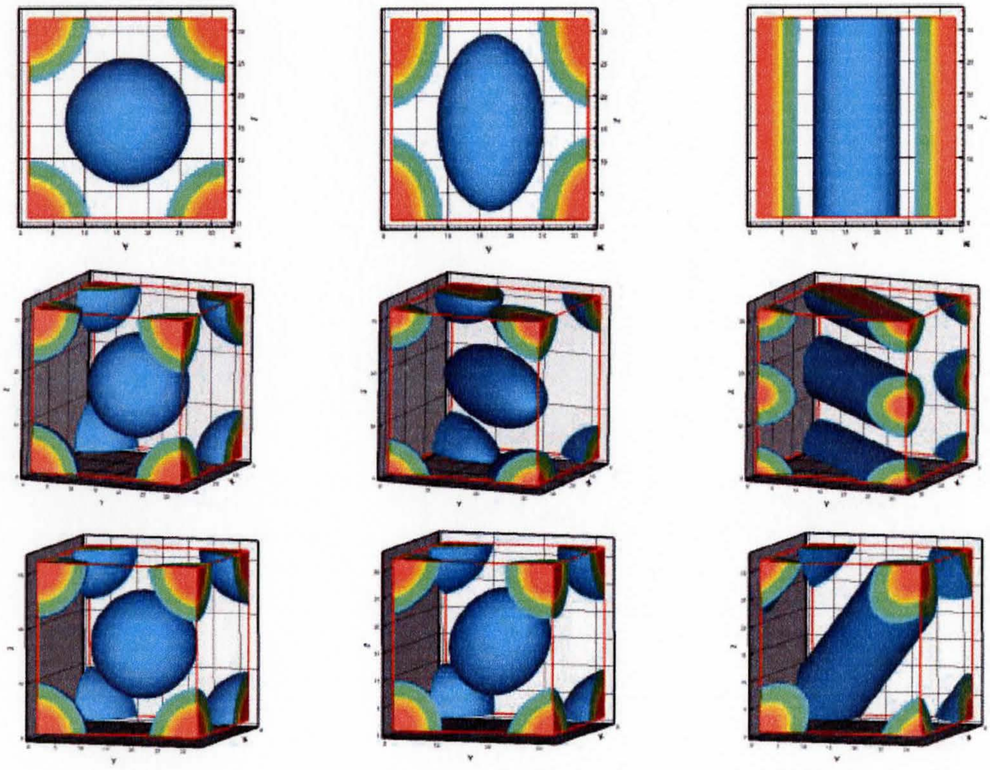


Figure 1.4: Deformation of the BCC morphology as the electric is applied along the (0, 0, 1), (1, 1, 0), (1, 1, 1) direction from top to bottom respectively. The strength of the electric field is increased form left to right. Calculations done by Jiang el al [26] [Courtesy of Jiang]

electrostatic energy consistent with it. It is valid close to the order-disorder transition [28]. The bulk diblock copolymer energy per polymer chain in units of k_BT in the absence of the electric field, F_b, and the electrostatic energy contribution, F_{es} are given as

$$F_b = \frac{1}{\Omega}\int\left\{\frac{1}{2}\tau\phi^2 + \frac{1}{2}h(\nabla^2\phi + q_0^2\phi)^2 + \frac{\lambda}{6}\phi^3 + \frac{u}{24}\phi^4\right\}d^3r, \tag{1.2}$$

$$F_{es} = -\frac{\epsilon_0\nu_p}{2k_BT\Omega}\int\kappa(\mathbf{r})[\nabla\psi(\mathbf{r})]^2d^3r. \tag{1.3}$$

The coefficients in F_b are given by

$$\begin{aligned} \tau &= \frac{2N(\chi_s - \chi)}{c^2}, \\ q_0 &\sim \frac{1}{R_g} = \left(\frac{1}{6}Nb^2\right)^{-\frac{1}{2}}, \\ h &= \frac{3}{2}\frac{R_g^2}{q_0^2}, \end{aligned}$$

where $N\chi_s$ is the spinodal value of χN, c is a constant of order 1, b is the Kuhn length, R_g is the radius of gyration, q_0 is the critical wave length, and λ and u are determined by f.

$F_{tot} = F_b + F_{es}$ is the free energy per polymer chain when an external electric field is applied. Obviously, the electrostatic potential should satisfy the usual Maxwell equation.

The local dielectric constant $\kappa(\mathbf{r})$ depends on the local concentration of monomers. In what follows, a simple linear constitutive relationship is used,

$$\kappa(\mathbf{r}) = <\kappa> + \phi(\mathbf{r})\Delta\kappa, \tag{1.4}$$

where $\Delta\kappa \equiv \kappa_A - \kappa_B, <\kappa> = f\kappa_A + (1-f)\kappa_B$.

Starting with a BCC phase and taking $\mathbf{E_0}$ to be in the (1, 1, 1) direction, the central idea used by Tsori et al is to write the concentration profile as

$$\phi = \omega\phi_1 + g\phi_2, \tag{1.5}$$

where the two basis functions are specified by

$$\phi_1 = \sum_{i=1}^{3} \cos(\mathbf{q_i} \cdot \mathbf{r}), \qquad \phi_2 = \sum_{i=1}^{3} \cos(\mathbf{k_i} \cdot \mathbf{r}). \tag{1.6}$$

The reciprocal lattice vectors $\mathbf{q_i}$ and $\mathbf{k_i}$ are

$$\mathbf{q_1} = \frac{q_0}{\sqrt{2}}(-1,0,1), \qquad \mathbf{q_2} = \frac{q_0}{\sqrt{2}}(1,-1,0), \qquad \mathbf{q_3} = \frac{q_0}{\sqrt{2}}(0,1,-1),$$

$$\mathbf{k_1} = \frac{q_0}{\sqrt{2}}(1,0,1), \qquad \mathbf{k_2} = \frac{q_0}{\sqrt{2}}(1,1,0), \qquad \mathbf{k_1} = \frac{q_0}{\sqrt{2}}(0,1,1). \tag{1.7}$$

As can be seen, the three $\mathbf{q_i}$ are orthogonal to the (1, 1, 1) axis and the three $\mathbf{k_i}$ have equal projection on the (1, 1, 1) direction. When $\omega = g$ in Equation (1.5), the density profile represents a BCC structure with the space group $Im\bar{3}m$. It is assumed that when an electric field is applied to the bcc phase, the resulting structure will have the $R\bar{3}m$ symmetry, thus the ϕ_1 and ϕ_2 have different coefficients $\omega \neq g$. With ω and g taking different values, this concentration profile can represent different phases including the BCC phase ($\omega = g$), a distorted BCC phase with $R\bar{3}m$ symmetry ($\omega \neq g$), a hexagonally packed cylindrical phase ($\omega \neq 0, g = 0$), and a disordered phase ($\omega = g = 0$). These phases are related to each other epitaxially. By following symmetry assumption, the local deviation of electric field from the average $\delta\mathbf{E} = \mathbf{E} - \mathbf{E_0}$ can be written in a similar form,

$$\delta\mathbf{E} = \alpha\mathbf{E_1} + \beta\mathbf{E_2},$$

$$\mathbf{E_1} = E_0 \sum_{i=1}^{3} \hat{\mathbf{q}}_\mathbf{i} \cos(\mathbf{q_i} \cdot \mathbf{r}), \qquad \mathbf{E_2} = E_0 \sum_{i=1}^{3} \hat{\mathbf{k}}_\mathbf{i} \cos(\mathbf{k_i} \cdot \mathbf{r}). \tag{1.8}$$

By inserting the expression of ϕ and $\delta\mathbf{E}$ into the Maxwell equation, the values of $\alpha(\omega, g)$ and $\beta(\omega, g)$ can be determined[27]. Then, the total free energy can be written as

$$\begin{aligned} F_{tot} = & + \frac{3}{4}\tau(\omega^2+g^2) + \frac{1}{4}\lambda\omega(3g^2+\omega^2) + \frac{15}{64}u(g^4+4g^2\omega^2+\omega^4) \\ & + \left[\frac{(\Delta\kappa)^2}{(2<\kappa> +\omega\Delta\kappa)}g^2 - \frac{1}{2}<\kappa>\right]\hat{E_0}^2, \end{aligned} \tag{1.9}$$

where $\hat{E}_0$ is the applied field in the natural unit,

$$\hat{E}_0 = (\frac{\epsilon_0 v_p}{k_B T})^{1/2}\mathbf{E_0}. \tag{1.10}$$

At a given external field and polymer architecture f, minimizing the total free energy with respect to ω and g , one can get stable phase structures. In Figure 1.5, the solid lines are the prediction of one-mode approximation, while the dashed lines are obtained with SCFT calculation. The ω and g value are normalized by their zero-field value. The increase of ω value and the decrease of the g value as the amplitude of electric field become larger means that the spheres turn into ellipsoids with the long axis in the direction of electric field. At certain magnitude of electric field, the g value drops to zero while the ω value attains a fixed value. This indicate that the structure becomes cylinders oriented along the electric field.

A phase diagram in the $(\chi/\chi_t, \hat{E}_0/E_t)$ rescaled plane for a fixed value of polymer architecture is illustrated in Figure 1.6. A distorted BCC region is confined between two lines of phase transitions. The other two phases are the disordered phase and the cylindrical phase. As the electric field increase, the distorted BCC region reduces and terminates at the triple point. The general features of the SCFT and one-mode results are consistent, as shown by Tsori et al [27].

The simple theory presented above captures the elongation of the sphere along the direction of the applied field, as well as the essence of the phase diagram. On the other hand, the structural change is assumed to follow a specific pathway. Although this assumption is reasonable, this a priori assumption is based on intuition. For

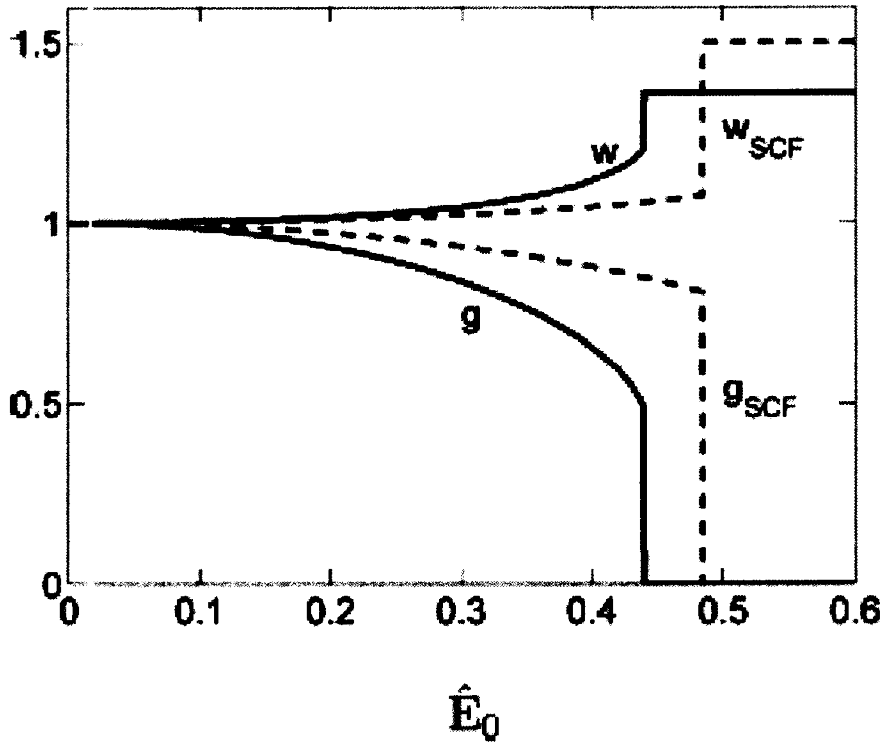


Figure 1.5: The change of the normalized value of ω and g as the electric field is increased in nature unit. Both the result from the single-mode approximation (solid lines) and the SCFT result (dashed lines) are showed. (Adopted from [27]).

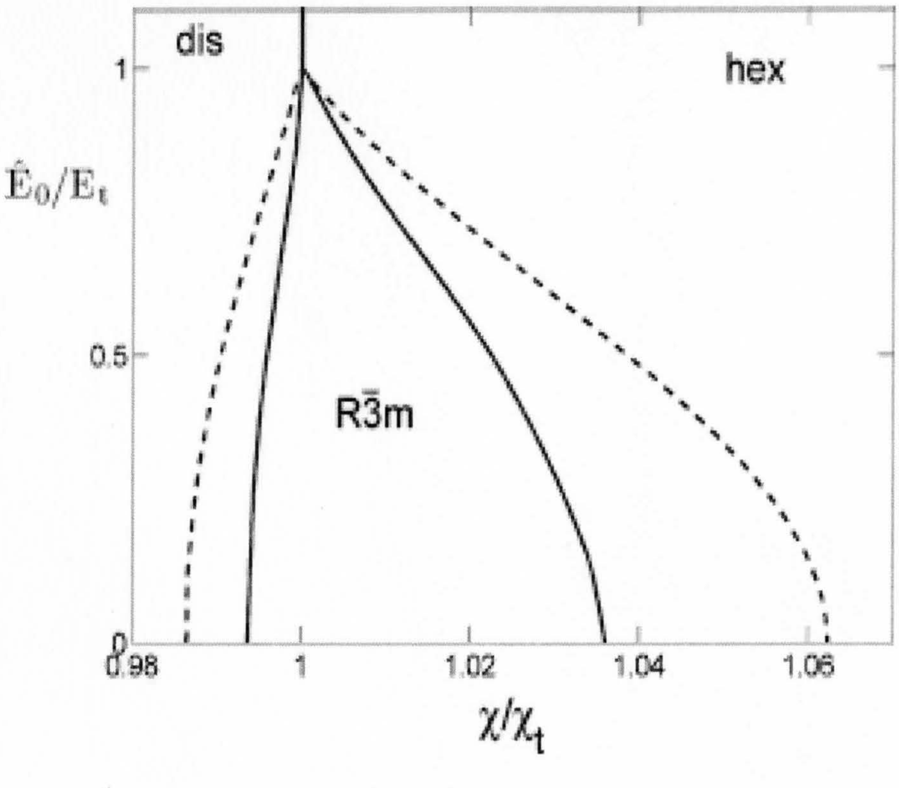


Figure 1.6: Phase diagram in the rescaled plane for diblocks with $f = 0.3$. The solid lines are form the single-mode approximation. The dashed lines are from the the SCFT calculation. (Adopted from [27]).

more complex structures and field orientation, it is not obvious how to write down the structural change pathways. Therefore, it is desirable to develop a method to predict the structural change.

In this thesis, a method to analyze the effect of external fields on the structural change of ordered phase is developed by taking the external field as a perturbation. The response of the density functional to the external field is given by the response function $R(\vec{r}, \vec{r'})$, which is related to the two-point correlation function $C(\vec{r}, \vec{r'})$. Unlike the real space calculation which is accurate but can not tell us why the structures change along certain pathways, and the single-mode approximation method which need to assume path ways, our theory has the advantage that one can predict the structural changes.

Furthermore, our perturbation theory is applied to the Landau-Brazovskii model. We analyzed the structure change of a BCC phase when the electric filed is applied along the (1, 1, 0) and (1, 1, 1) directions. Our results are compared with results of the other theoretical approaches.

Chapter 2

Theory

2.1 Introduction

This chapter covers the perturbation theory that we use to analyze the response of the order parameter of an ordered phase to the external fields. Also, application of the perturbation theory to the Landau-Brazovskii theory is introduced, including the properties of the two point correlation function $C(\vec{r},\vec{r'})$

2.2 Perturbation method

Consider a model system with a free energy functional $F(\{\phi(\vec{r})\})$, where $\phi(\vec{r})$ is the order parameter describing the state of the system. For block copolymers, this order parameter is usually taken as the density profile of the monomers. The equilibrium phases of this model system is determined by minimizing the free energy with respect to the order parameter. In another word, the mean field solution $\phi^{(0)}(\vec{r})$ are determined by solving the Euler-Lagrange equation

$$\left.\frac{\delta F(\{\phi(\vec{r})\})}{\delta\phi(\vec{r})}\right|_{\phi(\vec{r})=\phi^{(0)}(\vec{r})} = 0. \tag{2.1}$$

When an external field is applied to the system, the free energy has an additional term $V(\{\phi(\vec{r})\})$ due to the field. The solution is now determined by minimizing the total free energy

$$\frac{\delta[F(\{\phi(\vec{r})\}) + V(\{\phi(\vec{r})\})]}{\delta\phi(\vec{r})} = 0, \tag{2.2}$$

The basic idea of a perturbation method to solve this equation is to write the solution in the form

$$\phi(\vec{r}) = \phi^{(0)}(\vec{r}) + \delta\phi(\vec{r}), \tag{2.3}$$

where $\phi^{(0)}(\vec{r})$ is the solution for the case without the external potential and $\delta\phi(\vec{r})$ is the change of the solution due to the external field. Assuming that the change is small, we can expand the free energy around the mean-field solution, leading to the expression

$$F(\{\phi(\vec{r})\}) = F(\{\phi^{(0)}(\vec{r})\}) + \frac{1}{2}\int d\vec{r}d\vec{r'}\delta\phi(\vec{r})C(\vec{r},\vec{r'})\delta\phi(\vec{r'}) + \cdots, \tag{2.4}$$

where the first-order term vanishes since $\phi^{(0)}(\vec{r})$ is the mean-field solution. The two-point correlation function $C(\vec{r},\vec{r'})$ is given by

$$C(\vec{r},\vec{r'}) = \left.\frac{\delta^2 F(\{\phi(\vec{r})\})}{\delta\phi(\vec{r})\delta\phi(\vec{r'})}\right|_{\phi(\vec{r})=\phi^{(0)}(\vec{r})}. \tag{2.5}$$

The properties of the two-point correlation function for ordered phases has been analyzed by Shi [29]. The free energy contribution from the external field term can be expanded similarly

$$V(\{\phi(\vec{r})\}) = V(\{\phi^{(0)}(\vec{r})\}) + \int d\vec{r}\delta V(\vec{r})\delta\phi(\vec{r}) + \cdots, \tag{2.6}$$

where the linear external field term $\delta V(\vec{r})$ is given by

$$\delta V(\vec{r}) = \left.\frac{\delta V(\{\phi(\vec{r})\})}{\delta\phi(\vec{r})}\right|_{\phi(\vec{r})=\phi^{(0)}(\vec{r})}. \tag{2.7}$$

Minimizing the total free energy leads to an equation determining the response of the solution to the external field

$$\int d\vec{r'}C(\vec{r},\vec{r'})\delta\phi(\vec{r'}) + \delta V(\vec{r}) = 0. \tag{2.8}$$

Therefore to the lowest order, the external field will lead to a change of the solution in the form

$$\delta\phi(\vec{r}) = -\int d\vec{r'}C^{-1}(\vec{r},\vec{r'})\delta V(\vec{r'}), \tag{2.9}$$

where $C^{-1}(\vec{r},\vec{r'})$ is the inverse operator of $C(\vec{r},\vec{r'})$, which can be taken as the linear response function $R(\vec{r},\vec{r'})$.

For an ordered phase, the mean-field solution of the order parameter $\phi^{(0)}(\vec{r})$ is a periodic function. An ordered periodic structure can be described by a set of reciprocal lattice vectors, $\{\vec{G}\}$. Our task is to predict how this periodic function would change in the presence of an external field. Let us assume that the mean-field solution for the theory without external potential has the form

$$\phi^{(0)}(\vec{r}) = \sum_{\vec{G}} \phi(\vec{G})e^{i\vec{G}\cdot\vec{r}}. \tag{2.10}$$

The idea is then to write the modified solution with the linear response to the external field in the form

$$\phi^{(0)}(\vec{r}) + \delta\phi(\vec{r}) = \sum_{\vec{G}} \phi(\vec{G})e^{i\vec{G}\cdot\vec{r}} - \int d\vec{r'}C^{-1}(\vec{r},\vec{r'})\delta V(\vec{r'}) \approx \sum_{\vec{G'}} \phi(\vec{G'})e^{i\vec{G'}\cdot\vec{r}}. \tag{2.11}$$

If we can identify the new set of reciprocal lattice vectors $\{\vec{G'}\}$ and the corresponding coefficients $\phi(\vec{G'})$, we can predict the structural change.

In order to proceed, we can use the fact that the eigenfunctions of $C(\vec{r},\vec{r'})$ are Bloch functions of the form [29]

$$\Psi_{n\vec{k}}(\vec{r}) = e^{i\vec{k}\cdot\vec{r}}\sum_{\vec{G}} u_{n\vec{k}}(\vec{G})e^{i\vec{G}\cdot\vec{r}}, \tag{2.12}$$

where n is a band-index and $\vec{k}$ is a wave vector within the first Brillourn zone. These Bloch functions form a compete basis. This allows us to write the two-point correlation function in the form

$$C(\vec{r},\vec{r'}) = \sum_{n,\vec{k}} \lambda_n(\vec{k}) \Psi_{n\vec{k}}(\vec{r}) \Psi^*_{n\vec{k}}(\vec{r'}), \tag{2.13}$$

where $\lambda_n(\vec{k})$ are the eigenvalues of the two-point correlation function, and $\Psi_{n\vec{k}}(\vec{r})$ are the corresponding eigenfunctions. These quantities are determined from the equation

$$\int d\vec{r'} C(\vec{r},\vec{r'}) \Psi_{n\vec{k}}(\vec{r'}) = \lambda_n(\vec{k}) \Psi_{n\vec{k}}(\vec{r}). \tag{2.14}$$

The eigenfunctions satisfy the orthonormal and completeness conditions

$$\begin{aligned} \int \Psi_{n\vec{k}}(\vec{r}) \Psi^*_{n'\vec{k'}}(\vec{r}) &= \delta_{n,n'} \delta(\vec{k} - \vec{k'}), \\ \sum_{n,\vec{k}} \Psi_{n\vec{k}}(\vec{r}) \Psi^*_{n\vec{k}}(\vec{r'}) &= \delta(\vec{r} - \vec{r'}). \end{aligned}$$

Using the above expressions, the effect due to the external field can be written in the form

$$\begin{aligned} \phi^{(0)}(\vec{r}) + \delta\phi(\vec{r}) &= \sum_{\vec{G}} \phi(\vec{G}) e^{i\vec{G}\cdot\vec{r}} - \int d\vec{r'} \sum_{n,\vec{k}} \lambda_n^{-1}(\vec{k}) \Psi_{n\vec{k}}(\vec{r}) \Psi^*_{n\vec{k}}(\vec{r}) \delta V(\vec{r'}) \\ &= \sum_{\vec{G}} \phi(\vec{G}) e^{i\vec{G}\cdot\vec{r}} - \sum_{n,\vec{k}} \lambda_n^{-1}(\vec{k}) \Psi_{n\vec{k}}(\vec{r}) \int d\vec{r'} \Psi^*_{n\vec{k}}(\vec{r'}) \delta V(\vec{r'}) \\ &= \sum_{\vec{G}} \phi(\vec{G}) e^{i\vec{G}\cdot\vec{r}} - \sum_{n,\vec{k}} \lambda_n^{-1}(\vec{k}) \Psi_{n\vec{k}}(\vec{r}) \delta V_n(\vec{k}) \\ &= \sum_{\vec{G}} \phi(\vec{G}) e^{i\vec{G}\cdot\vec{r}} - \sum_{\vec{G}} \sum_{n,\vec{k}} \frac{\delta V_n(\vec{k}) u_{n\vec{k}}(\vec{G})}{\lambda_n(\vec{k})} e^{i(\vec{k}+\vec{G})\cdot\vec{r}}, \end{aligned}$$

where $\delta V_n(\vec{k})$ is the expansion coefficients of the external field

$$\delta V_n(\vec{k}) = \int d\vec{r'} \Psi^*_{n\vec{k}}(\vec{r'}) \delta V(\vec{r'}). \tag{2.15}$$

From the above expression, it is obvious that the most important contribution is from the term with the largest value of $\delta V_n(\vec{k})u_{n\vec{k}}(\vec{G})/\lambda_n(\vec{k})$, which is assumed to be at $n = n_0$ and $\vec{k} = \vec{k}_0$. If we only consider the largest contribution, we have

$$\begin{aligned}\phi^{(0)}(\vec{r}) + \delta\phi(\vec{r}) &\approx \sum_{\vec{G}} \phi(\vec{G})e^{i\vec{G}\cdot\vec{r}} - \lambda_{n_0}^{-1}(\vec{k}_0)\Psi_{n_0\vec{k}_0}(\vec{r})\delta V_{n_0}(\vec{k}_0) \\ &= \sum_{\vec{G}} \phi(\vec{G})e^{i\vec{G}\cdot\vec{r}} - \sum_{\vec{G}} \frac{\delta V_{n_0}(\vec{k}_0)}{\lambda_{n_0}(\vec{k}_0)} u_{n_0\vec{k}_0}(\vec{G})e^{i(\vec{k}_0+\vec{G})\cdot\vec{r}}. \qquad (2.16)\end{aligned}$$

Therefore, besides a change in the Fourier component $\phi(\vec{G})$, the external field may lead to new reciprocal lattice vectors of the form $\vec{G} + \vec{k}_0$.

This perturbation theory is general, applicable to any statistical systems. In what follows we will apply this method to the structural change of diblock copolymers in the presence of an applied electric field.

2.3 Application to Block copolymers in an electric field

For diblock copolymers, the Landau-Brazovskii theory is a simple theory to study their phase transitions. In this section, the structural change of diblock copolymer in the presence of an applied electric field is studied using the Landau-Brazovskii theory for weak crystallization and the perturbation method outlined above. Futhermore, the solution is obtained directly from the perturbation theory without explicitly using the correlation function. It is simpler to follow this route for the Landau-Brazovskii model.

For diblock copolymers, the order parameter $\phi(\vec{r})$ characterizes the deviation of the normalized A-monomer concentration form the uniform state, $\phi(r) = \phi_A(\vec{r}) - f_A$. This implies that the order parameter is constrained by $\int d^3r\phi(\vec{r}) = 0$. The Landau-

Brazovskii free energy per polymer chain in units of k_BT is [10], [11]

$$F_0(\phi) = \frac{1}{\Omega}\int d^3r\left\{\frac{\xi_0^2}{8q_0^2}[(\nabla^2+q_0^2)\phi(\vec{r})]^2 + \frac{\tau_0}{2}[\phi(\vec{r})]^2 - \frac{\gamma_0}{6}[\phi(\vec{r})]^3 + \frac{\lambda_0}{24}[\phi(\vec{r})]^4\right\}, \tag{2.17}$$

where ξ_0 is the bare correlation length, q_0 is the critical wave length, τ_0 is the reduced temperature, and γ_0 and λ_0 are expansion coefficients determined by f_A, Ω is the system volume. By using q_0^{-1} as the length scale, and λ_0 as the free energy scale, the coefficients can be rescaled as

$$F = q_0^3F_0/\lambda_0, \quad \xi = (q_0\xi_0)^2/(4\lambda_0),$$

$$\tau = \tau_0/\lambda_0, \qquad \gamma = \gamma_0/\lambda_0,$$

we can rewrite the free energy as

$$F = \frac{1}{\Omega}\int d^3r\left\{\frac{\xi^2}{2}[(\nabla^2+1)\phi(\vec{r})]^2 + \frac{\tau}{2}[\phi(\vec{r})]^2 - \frac{\gamma}{6}[\phi(\vec{r})]^3 + \frac{1}{24}[\phi(\vec{r})]^4\right\}, \tag{2.18}$$

where the scaled coefficients are determined by χN and f for diblock copolymers[30], [31].

When the diblock copolymers are placed in an external electric field $\mathbf{E_0}$. there is a electrostatic energy contribution to the total free energy per polymer chain as described in Chapter 1,

$$F_{es} = -\frac{\epsilon_0\nu_p}{2k_BT\Omega}\int \kappa(\vec{r})[\mathbf{E}(\vec{r})]^2d^3r, \tag{2.19}$$

where $\mathbf{E}(\vec{r}) = -\nabla\psi(\vec{r})$ is the local electric field, ϵ_0 is the vacuum permittivity, ν_p is the volume per chain segment, $\kappa(\vec{r}) =< \kappa > +\phi(\vec{r})\Delta\kappa$ is an effective dielectric constant.

The total free energy per polymer chain in units of k_BT is written as

$$\begin{aligned} F_{tot} = &+ \frac{\lambda_0}{q_0^3\Omega}\int d^3r\left\{\frac{\xi^2}{2}[(\nabla^2+1)\phi(\vec{r})]^2 + \frac{\tau}{2}[\phi(\vec{r})]^2 - \frac{\gamma}{6}[\phi(\vec{r})]^3 + \frac{1}{24}[\phi(\vec{r})]^4\right\} \\ &- \frac{\epsilon_0\nu_p}{2k_BT\Omega}\int \kappa(\vec{r})[\nabla\psi(\vec{r})]^2d^3r, \end{aligned} \tag{2.20}$$

where the first part is the Landau-Brazovskii free energy with scaled coefficients. The second part is the electrostatic energy contribution. The mean field solution is determined by minimizing this free energy.

Meanwhile, the solution $\phi(\vec{r})$ has to satisfy the incompressible condition $\int d^3r\phi(\vec{r}) = 0$. We can introduce a Lagrange Multiplier μ to enforce this constraint. To this end, we can rewrite the total free energy as

$$W = F_{tot} - \mu \int d^3r\phi(\vec{r}), \tag{2.21}$$

the value of μ is determined by $\int \phi(\vec{r})d^3r = 0$.

The mean-field equilibrium phase is determined by minimizing the total free energy functional W with respect to $\phi(\vec{r})$, $\psi(\vec{r})$ and μ,

$$\frac{\delta W}{\delta\phi(\vec{r})} = 0, \tag{2.22}$$

$$\frac{\delta W}{\delta\psi(\vec{r})} = 0, \tag{2.23}$$

$$\frac{\delta W}{\delta\mu} = 0. \tag{2.24}$$

These three equations leads to the following set of Euler-Lagrange equations:

$$\tau\phi(\vec{r})+\xi^2[\nabla^2+1]^2\phi(\vec{r})-\frac{\gamma}{2}[\phi(\vec{r})]^2+\frac{1}{6}[\phi(\vec{r})]^3-\frac{\epsilon_0\nu_p q_0^3}{2k_BT\lambda_0}\Delta\kappa[\nabla\psi(\vec{r})]^2-\mu\frac{\Omega q_0^3}{\lambda_0} = 0, \tag{2.25}$$

$$\nabla\cdot[\{<\kappa> +\Delta\kappa\phi(\vec{r})\}\nabla\psi(\vec{r})] = 0, \tag{2.26}$$

$$\int d^3r\phi(\vec{r}) = 0. \tag{2.27}$$

This set of equations determines the mean-field solutions in the existence of the applied electric field $\vec{E_0}$. In particular, the second equation is the Poisson equation determining the electrostatic potential. For the case of a fixed applied electric field, the electric field can be written as

$$\vec{E} = -\nabla\psi = \vec{E_0} - \nabla\delta\psi(\vec{r}). \tag{2.28}$$

The mean-field equations become

$$\tau\phi(\vec{r})+\xi^2[\nabla^2+1]^2\phi(\vec{r})-\frac{\gamma}{2}[\phi(\vec{r})]^2+\frac{1}{6}[\phi(\vec{r})]^3-\frac{\epsilon_0\nu_p q_0^3}{2k_BT\lambda_0}\Delta\kappa[\nabla\delta\psi(\vec{r})-\vec{E}_0]^2-\mu\frac{\Omega q_0^3}{\lambda_0}=0, \tag{2.29}$$

$$\nabla\cdot[\{<\kappa>+\Delta\kappa\phi(\vec{r})\}\{\nabla\delta\psi(\vec{r})-\vec{E}_0]=0. \tag{2.30}$$

The second equation for the electrostatic potential can be written explicitly as

$$<\kappa>\nabla^2\delta\psi(\vec{r})+\Delta\kappa\nabla\cdot[\phi(\vec{r})\nabla\delta\psi(\vec{r})]=\Delta\kappa\vec{E}_0\cdot\nabla\phi(\vec{r}). \tag{2.31}$$

This equation shows that the deviation of the potential $\delta\psi(\vec{r})$ is due to the coupling of the applied field and the order parameter. The electric field term can be viewed as a source term in the first mean-field equation

$$\tau\phi(\vec{r})+\xi^2[\nabla^2+1]^2\phi(\vec{r})-\frac{\gamma}{2}[\phi(\vec{r})]^2+\frac{1}{6}[\phi(\vec{r})]^3=\frac{\epsilon_0\nu_p q_0^3}{2k_BT\lambda_0}\Delta\kappa[\nabla\delta\psi(\vec{r})-\vec{E}_0]^2+\mu\frac{\Omega q_0^3}{\lambda_0}. \tag{2.32}$$

To proceed, we assume that the applied field is weak and can be expanded around the mean-field solution without the applied field

$$\phi(\vec{r})=\phi^{(0)}(\vec{r})+\delta\phi(\vec{r}),$$

$$\mu=\mu_0+\delta\mu,$$

where μ_0 is the Lagrange multiplier corresponding to $\phi^{(0)}(\vec{r})$, $\delta\mu$ correspsing to the change of the Lagrange multiplier when the electric field is applied and the order parameter is changed by $\delta\phi(\vec{r})$. The zeroth order solution $\phi^{(0)}(\vec{r})$ satisfies the mean-field equation in the absence of the applied electric filed,

$$\tau\phi^{(0)}(\vec{r})+\xi^2[\nabla^2+1]^2\phi^{(0)}(\vec{r})-\frac{\gamma}{2}[\phi^{(0)}(\vec{r})]^2+\frac{1}{6}[\phi^{(0)}(\vec{r})]^3=\mu_0\frac{\Omega q_0^3}{\lambda_0}. \tag{2.33}$$

For the Landau-Brazovskii model, the solution of this equation will leads to a variety of periodic ordered phases[10], [11]

$$\phi^{(0)}(\vec{r})=\sum_{\vec{G}}\phi(\vec{G})e^{i\vec{G}\cdot\vec{r}}, \tag{2.34}$$

where the reciprocal lattice vectors $\{\vec{G}\}$ are determined by the symmetry of the ordered phase.

Expanding around the periodic solution, $\phi(\vec{r}) = \phi^{(0)}(\vec{r}) + \delta\phi(\vec{r})$, to the lowest order we have

$$\{\tau + \xi^2(\nabla^2+1)^2 - \gamma\phi^{(0)} + \frac{1}{2}[\phi^{(0)}(\vec{r})]^2\}\delta\phi(\vec{r}) = \frac{\epsilon_0 \nu_p q_0^3}{2k_B T\lambda_0}\Delta\kappa[\nabla\delta\psi(\vec{r}) - \vec{E}_0]^2 + \delta\mu\frac{\Omega q_0^3}{\lambda_0}, \tag{2.35}$$

$$< \kappa > \nabla^2\delta\psi(\vec{r}) + \Delta\kappa\nabla\cdot[\phi^{(0)}(\vec{r})\nabla\delta\psi(\vec{r})] = \Delta\kappa\vec{E}_0\cdot\nabla\phi^{(0)}(\vec{r}), \tag{2.36}$$

where it is assumed that the applied field is weak and the deviations of the order parameter and the static potential are of the order of E_0. Also we have the incompressible condition that

$$\int d^3r\delta\phi(\vec{r}) = 0. \tag{2.37}$$

The procedure of solving these equations is to obtain the static potential $\delta\psi(\vec{r})$ from the equation (2.36) first. The solution is then inserted to the equation (2.35) and combine with the equation(2.37) to obtain the solution of the order parameter $\delta\phi(\vec{r})$.

It is convenient to cast the equations in the Fourier space

$$\phi^{(0)}(\vec{r}) = \sum_{\vec{G}}\phi(\vec{G})e^{i\vec{G}\cdot\vec{r}},$$

$$\delta\phi(\vec{r}) = \int d^3k\delta\phi(\vec{k})e^{i\vec{k}\cdot\vec{r}},$$

$$\delta\psi(\vec{r}) = \int d^3k\delta\psi(\vec{k})e^{i\vec{k}\cdot\vec{r}}.$$

With these expressions equation (2.36) becomes

$$\begin{aligned} &- < \kappa > \int d^3k\vec{k}^2\delta\psi(\vec{k})e^{i\vec{k}\cdot\vec{r}} - \Delta\kappa\sum_{\vec{G}}\int d^3k\vec{k}\cdot(\vec{k}+\vec{G})\phi_{\vec{G}}\delta\psi(\vec{k})e^{i(\vec{k}+\vec{G})\cdot\vec{r}} \\ &= \Delta\kappa\sum_{\vec{G}}(i\vec{G}\cdot\vec{E}_0)\phi_{\vec{G}}e^{i\vec{G}\cdot\vec{r}}. \end{aligned} \tag{2.38}$$

Multiplying this equation with $e^{-\vec{q}\cdot\vec{r}}$ and integrate over $\vec{r}$, we have

$$< \kappa > q^2\delta\psi(\vec{q})+\Delta\kappa\sum_{\vec{G}}\vec{q}\cdot(\vec{q}-\vec{G})\phi_{\vec{G}}\delta\psi(\vec{q}-\vec{G}) = -i\Delta\kappa\sum_{\vec{G}}\vec{G}\cdot\vec{E}_0\phi_{\vec{G}}\delta(\vec{q}-\vec{G}). \quad (2.39)$$

This equation has non-zero solutions only when the wave vector $\vec{q}$ equals to one of the reciprocal lattice vectors, $\vec{q}=\vec{G}$. By solving the set of equations for different values of reciprocal vectors, values of $\delta\psi(\vec{G})$ can be obtained. The solution is then inserted into the right hand side of equation (2.35), which can be denoted as $S(\vec{r})$. $S(\vec{r})$ then can be expanded as

$$S(\vec{r}) = \sum_{\vec{G}} S(\vec{G})e^{i\vec{G}\cdot\vec{r}}. \quad (2.40)$$

Also, we can denote the operator applied to $\delta\phi(\vec{r})$ in the equation (2.35) as $\hat{C}(\vec{r})$.

$$\hat{C}(\vec{r}) = \tau + \xi^2(\nabla^2+1)^2 - \gamma\phi^{(0)} + \frac{1}{2}[\phi^{(0)}(\vec{r})]^2 = \tau + \xi^2(\nabla^2+1)^2 + V(\vec{r}). \quad (2.41)$$

Here $V(\vec{r}) = -\gamma\phi^{(0)} + \frac{1}{2}[\phi^{(0)}(\vec{r})]^2$. For an ordered structure, the potential $V(\vec{r})$ is a periodic function. The first equation can be written in a simple form

$$\hat{C}(\vec{r})\delta\phi(\vec{r}) = S(\vec{r}). \quad (2.42)$$

By casting this equation into the Fourier space,

$$\begin{aligned}
\phi^{(0)}(\vec{r}) &= \sum_{\vec{G}} \phi_G e^{i\vec{G}\cdot\vec{r}}, \\
V(\vec{r}) &= \sum_{\vec{G}} V(\vec{G})e^{i\vec{G}\cdot\vec{r}}, \\
\delta\phi(\vec{r}) &= \int d^3k\delta\phi(\vec{k})e^{i\vec{k}\cdot\vec{r}}, \\
S(\vec{r}) &= \sum_{\vec{G}} S(\vec{G})e^{i\vec{G}\cdot\vec{r}},
\end{aligned}$$

the equation becomes

$$[\tau + \xi^2(\nabla^2+1)^2 + \sum_{\vec{G}} V(\vec{G})e^{i\vec{G}\cdot\vec{r}}]\int d^3k\delta\phi(\vec{k})e^{i\vec{k}\cdot\vec{r}} = \sum_{\vec{G}} S(\vec{G})e^{i\vec{G}\cdot\vec{r}}, \quad (2.43)$$

which can be written in the form

$$\int d^3k[\tau + \xi^2(k^2-1)^2 + \sum_{\vec{G}} V(\vec{G})e^{i\vec{G}\cdot\vec{r}}]\delta\phi(\vec{k})e^{i\vec{k}\cdot\vec{r}} = \sum_{\vec{G}} S(\vec{G})e^{i\vec{G}\cdot\vec{r}}. \tag{2.44}$$

Multiplying this equation with $e^{-i\vec{q}\cdot\vec{r}}$ and integrate over $\vec{r}$, we have

$$[\tau + \xi^2(q^2-1)^2]\delta\phi(\vec{q}) + \sum_{\vec{G}} V(\vec{G})\delta\phi(\vec{q}-\vec{G}) = \sum_{\vec{G}} S(\vec{G})\delta(\vec{q}-\vec{G}). \tag{2.45}$$

The solution would be zero if $\vec{q}$ is not one of the reciprocal lattice vectors. For $\vec{q}=\vec{G}$, we have

$$[\tau + \xi^2(\vec{G}^2-1)^2]\delta\phi(\vec{G}) + \sum_{\vec{G}'} V(\vec{G}-\vec{G}')\delta\phi(\vec{G}') = S(\vec{G}). \tag{2.46}$$

This equation can be written in terms of the correlation function $C(\vec{G},\vec{G}')$,

$$\sum_{\vec{G}'} C(\vec{G},\vec{G}')\delta\phi(\vec{G}') = S(\vec{G}), \tag{2.47}$$

where the correlation function is a matrix defined by

$$C(\vec{G},\vec{G}') = [\tau + \xi^2(\vec{G}^2-1)^2]\delta(\vec{G}-\vec{G}') + V(\vec{G}-\vec{G}'). \tag{2.48}$$

Here the value of $V(\vec{G}-\vec{G}')$ can be get when we expand the potential $V(\vec{r})$ as

$$V(\vec{r}) = \sum_{\vec{G}} V(\vec{G})e^{i\vec{G}\cdot\vec{r}}.$$

$V(\vec{r})$ is given in terms of the mean-field solution

$$V(\vec{r}) = -\gamma\phi^{(0)}(\vec{r}) + \frac{1}{2}[\phi^{(0)}(\vec{r})]^2.$$

Expanding $\phi^{(0)}(\vec{r})$ as $\phi^{(0)}(\vec{r}) = \sum_{\vec{G}}\phi_G e^{i\vec{G}\cdot\vec{r}}$, we get

$$V(\vec{r}) = \sum_{\vec{G}}[-\gamma\phi_G + \frac{1}{2}\sum_{\vec{G}'}\phi_{G-G'}\phi_{G'}]e^{i\vec{G}\cdot\vec{r}}. \tag{2.49}$$

So we have

$$V(\vec{G}) = -\gamma\phi_G + \frac{1}{2}\sum_{\vec{G}'}\phi_{G-G'}\phi_{G'}. \tag{2.50}$$

Then the matrix elements for $C(\vec{G},\vec{G}')$ can be calculated. Combine the matrix equation (2.47) and the incompressible condition (2.37) we can find the solution of $\delta\phi(\vec{G}')$.

It is worth to discuss the general case of structural change here. To solve $\delta\phi(\vec{r})$ which is determined by the equation

$$\hat{C}(\vec{r})\delta\phi(\vec{r}) = S(\vec{r}), \tag{2.51}$$

we can expand $\delta\phi(\vec{r}), S(\vec{r})$ by the eigenfunctions of $\hat{C}(\vec{r})$

$$\delta\phi(\vec{r}) = \sum_{n,\vec{k}} \delta\phi_{n\vec{k}}\Psi_{n\vec{k}}(\vec{r}), \tag{2.52}$$

$$S(\vec{r}) = \sum_{n\vec{k}} S_{n\vec{k}}\Psi_{n\vec{k}}(\vec{r}). \tag{2.53}$$

This leads to the solution

$$\begin{aligned} \delta\phi(\vec{r}) &= \sum_{n,\vec{k}} \frac{S_{n\vec{k}}}{\lambda_{n\vec{k}}}\Psi_{n\vec{k}}(\vec{r}) \\ &= \sum_{\vec{G}}\sum_{n,\vec{k}} \frac{S_{n\vec{k}}u_{n\vec{k}}(\vec{G})}{\lambda_{n\vec{k}}} e^{i(\vec{k}+\vec{G})\cdot\vec{r}}. \end{aligned} \tag{2.54}$$

If we only consider the largest contribution which is at $n = n_0, \vec{k} = \vec{k}_0$. Then

$$\delta\phi(\vec{r}) = \sum_{\vec{G}} \frac{S_{n_0\vec{k}_0}u_{n_0\vec{k}_0}(\vec{G})}{\lambda_{n_0\vec{k}_0}} e^{i(\vec{k}_0+\vec{G})\cdot\vec{r}}. \tag{2.55}$$

From this expression, it can be concluded that, in general, the external field may lead to new reciprocal lattice vectors of the form $\vec{G}+\vec{k}_0$. In the case $\vec{k}_0 = 0$, the reciprocal lattice vectors remain the same. Only the amplitude of the expansion coefficients change.

In the electric field case, the source term $S(\vec{r})$ can be expanded as $S(\vec{r}) = \sum_{\vec{G}} S(\vec{G})e^{i\vec{G}\cdot\vec{r}}$. This leads to $\delta\phi(\vec{r}) = \sum_{\vec{G}} \delta\phi(\vec{G})e^{i\vec{G}\cdot\vec{r}}$, which means $k = 0$. In this case, the structural change is an epitaxial change[32].

Chapter 3

Implementation: One-mode approximation

In this chapter, we show how the method described above can be applied to the structure change of the body-centered-cubic phase in the presence of an applied electric field. All the parameters used here are taken to be the same as those used in the single-mode approximation [27]. For a body-centered-cubic phase, the reciprocal lattice vectors are on a face-centered-cubic structure. The mean field order parameter can be expanded in terms of reciprocal vectors

$$\phi^{(0)}(\vec{r}) = \sum_{\{\vec{G}\}} \phi_{\vec{G}} e^{i\vec{G}\cdot\vec{r}}. \tag{3.1}$$

For the density modulation, the order parameter is real, we have $\phi_{-\vec{G}} = \phi^*_{\vec{G}}$. The Landau-Brazobskii free energy density can be rewritten in terms of $\phi_{\vec{G}}$ as

$$F_0 = \frac{1}{2}\sum_{\vec{G}}[\xi^2(\vec{G}^2 - -1)^2 + \tau]|\phi_{\vec{G}}|^2 - \frac{\gamma}{6}\sum_{\vec{G}_1,\vec{G}_2} \phi_{\vec{G}_1}\phi_{\vec{G}_2}\phi^*_{\vec{G}_1+\vec{G}_2} + \frac{1}{24}\sum_{\vec{G}_1,\vec{G}_2,\vec{G}_3} \phi_{\vec{G}_1}\phi_{\vec{G}_2}\phi_{\vec{G}_3}\phi^*_{\vec{G}_1+\vec{G}_2+\vec{G}_3}. \tag{3.2}$$

Because the ordered structure has rotational symmetry, the reciprocal vectors are related by the point group symmetry and can be grouped into stars[29]. The Fourier coefficients for the nth star are not independent and they are related by

$$\phi_{\vec{G_i^n}} = \frac{S_i^n}{\sqrt{N_n}} A_n, \tag{3.3}$$

where $|\vec{G_i^n}|^2 = \lambda_n$, and S_i^n is determined by the symmetry of the structure. The Fourier expansion of the orderd parameter becomes

$$\phi^{(0)}(\vec{r}) = \sum_n A_n f_n(\vec{r}), \tag{3.4}$$

where the new basis function $f_n(\vec{r})$ is

$$f_n(\vec{r}) = \frac{1}{\sqrt{N_n}} \sum_i S_i^n A_n. \tag{3.5}$$

In terms of the coefficients A_n, the mean field free energy density is

$$F_0 = \frac{1}{2} \sum_n [\xi^2(\lambda_n - 1)^2 + \tau] A_n^2 - \frac{\gamma}{6} \sum_{n,m,l} \Gamma_{0nml} A_n A_m A_l + \frac{1}{24} \sum_{n,m,l,k} \Gamma_{nmlk} A_n A_m A_l A_k, \tag{3.6}$$

where the coefficients Γ_{nmkl} are given by

$$\Gamma_{nmkl} = \frac{1}{\sqrt{N_n N_m N_l N_k}} \sum_{i=1}^{n} \sum_{j=1}^{m} \sum_{s=1}^{l} \sum_{t=1}^{k} \delta_{G_i^n + G_j^m + G_s^l + G_t^k}. \tag{3.7}$$

As the Landua-Brazovskii free energy is valid close to the ODT point, for simplicity, we can use the set of shortest reciprocal vectors. In units of q_0, this set of basis vectors are of the unit length and can be represented as

$$\begin{array}{lll}
G_1^1 = \frac{1}{\sqrt{2}}(1,1,0), & G_2^1 = \frac{1}{\sqrt{2}}(-1,1,0), & G_3^1 = \frac{1}{\sqrt{2}}(-1,-1,0), \\
G_4^1 = \frac{1}{\sqrt{2}}(1,-1,0), & G_5^1 = \frac{1}{\sqrt{2}}(0,1,1), & G_6^1 = \frac{1}{\sqrt{2}}(0,-1,1), \\
G_7^1 = \frac{1}{\sqrt{2}}(0,-1,-1), & G_8^1 = \frac{1}{\sqrt{2}}(0,1,-1), & G_9^1 = \frac{1}{\sqrt{2}}(1,0,1), \\
G_{10}^1 = \frac{1}{\sqrt{2}}(1,0,-1), & G_{11}^1 = \frac{1}{\sqrt{2}}(-1,0,-1), & G_{12}^1 = \frac{1}{\sqrt{2}}(-1,0,1).
\end{array}$$

These 12 reciprocal lattice vectors are related by the point group symmetry of the cubic phase. The coefficients of the density profile are of the same value

$$\phi(G_i^1) = \frac{1}{\sqrt{N_1}} A_1 = \frac{1}{\sqrt{12}} A_1. \tag{3.8}$$

The basis functions can be grouped into one function as the first basis function for a bcc phase

$$f_1 = \frac{1}{\sqrt{N_1}} \sum_i e^{iG_i^1 \cdot r} = \frac{1}{\sqrt{12}} \sum_i e^{iG_i^1 \cdot r}. \tag{3.9}$$

Under this one mode approximation for bcc structure, the free energy density is

$$\begin{aligned} F_0^{bcc} &= \frac{\tau}{2} A_1^2 - \frac{\gamma}{6} \Gamma_{0111} A_1^3 + \frac{1}{24} \Gamma_{1111} A_1^4 \\ &= \frac{\tau}{2} A_1^2 - \frac{\gamma}{6} \sqrt{\frac{4}{3}} A_1^3 + \frac{1}{24} \frac{15}{4} A_1^4. \end{aligned} \tag{3.10}$$

We find that the minimum free energy occurs at

$$A_1 = \frac{4\sqrt{3}}{15} \gamma \left(1 + \sqrt{1 - \frac{15\tau}{2\gamma^2}}\right). \tag{3.11}$$

For $\vec{G}$ taking the 12 shortest wave vectors showed above and $\vec{G}_0 = (0, 0, 0)$, the matrix $\hat{C}(\vec{G}-\vec{G}')$ is a 13×13 symmetric matrix indexed by this thirteen reciprocal-lattice vectors. The $V(\vec{G} - \vec{G}')$ can have five different values, denoted as V_0, V_1, V_2, V_3, V_4, corresponding to $|\vec{G}-\vec{G}'| = 0, |\vec{G}-\vec{G}'| = 1, |\vec{G}-\vec{G}'| = \sqrt{2}, |\vec{G}-\vec{G}'| = \sqrt{3}, |\vec{G}-\vec{G}'| = 2$, respectively. By checking the reciprocal space with FCC structure, we find that there is one $\vec{G}$ with $|\vec{G}| = 0$, there are twelve $\vec{G}$'s with $|\vec{G}| = 1$, six $\vec{G}$'s with $|\vec{G}| = \sqrt{2}$, twenty-four $\vec{G}$'s with $|\vec{G}| = \sqrt{3}$, and twelve $\vec{G}$'s with $|\vec{G}| = 2$. The V's are calculated by using $V(\vec{G}) = -\gamma \phi_G + \frac{1}{2} \sum_{\vec{G}'} \phi_{G-G'} \phi_{G'}$. Under one mode approximation, there are twelve $\vec{G}'$'s which can give none zero value for $\phi_{G-G'}$ when $|\vec{G}| = 0$. There are four $\vec{G}'$'s which can give none zero value for $\phi_{G-G'}$ when $|\vec{G}| = 1$. There are four $\vec{G}'$'s which can give none zero value for $\phi_{G-G'}$ when $|\vec{G}| = \sqrt{2}$. There are two $\vec{G}'$'s which can give none zero value for $\phi_{G-G'}$ when $|\vec{G}| = \sqrt{3}$. There is one $\vec{G}'$ which can give none zero value for $\phi_{G-G'}$ when $|\vec{G}| = 2$.

For $|\vec{G} - \vec{G}'| = 0$,

$$V_0 = \frac{1}{2} * 12 * \frac{A_1}{\sqrt{12}} * \frac{A_1}{\sqrt{12}} = \frac{1}{2} A_1^2. \tag{3.12}$$

For $|\vec{G} - \vec{G'}| = 1$,

$$V_1 := -\gamma * \frac{A_1}{\sqrt{12}} + \frac{1}{2} * 4 * \frac{A_1}{\sqrt{12}} * \frac{A_1}{\sqrt{12}} = -\gamma \frac{A_1}{\sqrt{12}} + \frac{1}{6} A_1^2. \tag{3.13}$$

For $|\vec{G} - \vec{G'}| = \sqrt{2}$,

$$V_2 = \frac{1}{2} * 4 * \frac{A_1}{\sqrt{12}} * \frac{A_1}{\sqrt{12}} = \frac{1}{6} A_1^2. \tag{3.14}$$

For $|\vec{G} - \vec{G'}| = \sqrt{3}$,

$$V_3 = \frac{1}{2} * 2 * \frac{A_1}{\sqrt{12}} * \frac{A_1}{\sqrt{12}} = \frac{1}{12} A_1^2. \tag{3.15}$$

For $|\vec{G} - \vec{G'}| = 2$,

$$V_4 = \frac{1}{2} * 1 * \frac{A_1}{\sqrt{12}} * \frac{A_1}{\sqrt{12}} = \frac{1}{24} A_1^2. \tag{3.16}$$

The correlation matrix $C(\vec{r}, \vec{r'})$ is then given by

$$\begin{pmatrix}
H_0 & V_1 & V_1 & V_1 & V_1 & V_1 & V_1 & V_1 & V_1 & V_1 & V_1 & V_1 & V_1 \\
V_1 & H_1 & V_2 & V_4 & V_2 & V_1 & V_3 & V_3 & V_1 & V_1 & V_1 & V_3 & V_3 \\
V_1 & V_2 & H_2 & V_2 & V_4 & V_1 & V_3 & V_3 & V_1 & V_3 & V_3 & V_1 & V_1 \\
V_1 & V_4 & V_2 & H_3 & V_2 & V_3 & V_1 & V_1 & V_3 & V_3 & V_3 & V_1 & V_1 \\
V_1 & V_2 & V_4 & V_2 & H_4 & V_3 & V_1 & V_1 & V_3 & V_1 & V_1 & V_3 & V_3 \\
V_1 & V_1 & V_1 & V_3 & V_3 & H_5 & V_2 & V_4 & V_2 & V_1 & V_3 & V_3 & V_1 \\
V_1 & V_3 & V_3 & V_1 & V_1 & V_2 & H_6 & V_2 & V_4 & V_1 & V_3 & V_3 & V_1 \\
V_1 & V_3 & V_3 & V_1 & V_1 & V_4 & V_2 & H_7 & V_2 & V_3 & V_1 & V_1 & V_3 \\
V_1 & V_1 & V_1 & V_3 & V_3 & V_2 & V_4 & V_2 & H_8 & V_3 & V_1 & V_1 & V_3 \\
V_1 & V_1 & V_3 & V_3 & V_1 & V_1 & V_1 & V_3 & V_3 & H_9 & V_2 & V_4 & V_2 \\
V_1 & V_1 & V_3 & V_3 & V_1 & V_3 & V_3 & V_1 & V_1 & V_2 & H_{10} & V_2 & V_4 \\
V_1 & V_3 & V_1 & V_1 & V_3 & V_3 & V_3 & V_1 & V_1 & V_4 & V_2 & H_{11} & V_2 \\
V_1 & V_3 & V_1 & V_1 & V_3 & V_1 & V_1 & V_3 & V_3 & V_2 & V_4 & V_2 & H_{12}
\end{pmatrix}$$

where

$$H_0 = \xi^2 + \tau + V_0, \tag{3.17}$$

$$H_i = \tau + V_0, \tag{3.18}$$

for $i = 1$ to 12.

Now, we are in a position to solve the equation (2.39). For this equation to have non-zero solutions within the one-mode approximation, the wave vector $\vec{q}$ must be one of the twelve shortest basis vectors. Also, consistent with the one-mode approximation, we only solve $\delta\psi(\vec{G})$ for this twelve shortest basis vectors. This means we neglect $\delta\psi(\vec{q}-\vec{G})$ if $\vec{q}-\vec{G}$ is not one of the twelve shortest basis vectors. Then for $\vec{q}=\vec{G}_1$ and $\vec{q}=\vec{G}_2$ the equation (2.28) can be written as

$$\begin{aligned} <\kappa> \vec{G}_1^{\,2}\delta\psi(\vec{G}_1) &+ \Delta\kappa\vec{G}_1\cdot(\vec{G}_1-\vec{G}_5)\phi_{\vec{G}_5}\delta\psi(\vec{G}_{10}) + \Delta\kappa\vec{G}_1\cdot(\vec{G}_1-\vec{G}_8)\phi_{\vec{G}_8}\delta\psi(\vec{G}_9) \\ &+ \Delta\kappa\vec{G}_1\cdot(\vec{G}_1-\vec{G}_9)\phi_{\vec{G}_9}\delta\psi(\vec{G}_8) + \Delta\kappa\vec{G}_1\cdot(\vec{G}_1-\vec{G}_{10})\phi_{\vec{G}_{10}}\delta\psi(\vec{G}_5) \\ &= -i\Delta\kappa\vec{G}_1\cdot\vec{E}_0\phi_{\vec{G}_1}, \end{aligned} \tag{3.19}$$

$$\begin{aligned} <\kappa> \vec{G}_2^{\,2}\delta\psi(\vec{G}_2) &+ \Delta\kappa\vec{G}_2\cdot(\vec{G}_2-\vec{G}_5)\phi_{\vec{G}_5}\delta\psi(\vec{G}_{11}) + \Delta\kappa\vec{G}_2\cdot(\vec{G}_2-\vec{G}_8)\phi_{\vec{G}_8}\delta\psi(\vec{G}_{12}) \\ &+ \Delta\kappa\vec{G}_2\cdot(\vec{G}_2-\vec{G}_{12})\phi_{\vec{G}_{12}}\delta\psi(\vec{G}_8) + \Delta\kappa\vec{G}_2\cdot(\vec{G}_2-\vec{G}_{11})\phi_{\vec{G}_{11}}\delta\psi(\vec{G}_5) \\ &= -i\Delta\kappa\vec{G}_2\cdot\vec{E}_0\phi_{\vec{G}_2}. \end{aligned} \tag{3.20}$$

In general this set of equations has the form,

$$\begin{aligned} <\kappa> \vec{G}_i^{\,2}\delta\psi(\vec{G}_i) &+ \Delta\kappa\vec{G}_i\cdot(\vec{G}_i-\vec{G}_n)\phi_{\vec{G}_n}\delta\psi(\vec{G}_l) + \Delta\kappa\vec{G}_i\cdot(\vec{G}_i-\vec{G}_m)\phi_{\vec{G}_m}\delta\psi(\vec{G}_k) \\ &+ \Delta\kappa\vec{G}_i\cdot(\vec{G}_i-\vec{G}_k)\phi_{\vec{G}_k}\delta\psi(\vec{G}_m) + \Delta\kappa\vec{G}_i\cdot(\vec{G}_i-\vec{G}_l)\phi_{\vec{G}_l}\delta\psi(\vec{G}_n) \\ &= -i\Delta\kappa\vec{G}_i\cdot\vec{E}_0\phi_{\vec{G}_i}, \end{aligned} \tag{3.21}$$

where the values of n, k, m and l are given in Table 3.1 for $i = 1$ to 12 respectively.

By solving these twelve equations, we obtain $\delta\psi(\vec{G})$ for the twelve shortest basis

i	n	k	m	l
1	5	8	9	10
2	5	8	11	12
3	7	6	11	12
4	6	7	9	10
5	1	2	9	12
6	3	4	12	9
7	3	4	11	10
8	1	2	10	11
9	1	4	5	6
10	1	4	8	7
11	2	3	8	7
12	2	3	5	6

Table 3.1: Values of n, k, m and l in equation (3.21) for $i = 1$ to 12.

vectors

$$\begin{aligned}\delta\psi(\vec{G}_i) &= -\frac{i\Delta\kappa\phi_G}{(<\kappa> +\Delta\kappa\phi_G)}(\vec{G}_i\cdot\vec{E}_0) \\ &= -B(\vec{G}_i\cdot\vec{E}_0),\end{aligned} \tag{3.22}$$

where

$$B = \frac{i\Delta\kappa\phi_G}{(<\kappa> +\Delta\kappa\phi_G)}. \tag{3.23}$$

Then we can use these results to compute $S(\vec{r})$. Let $C = \frac{\epsilon_0 v_p q_0^3}{2k_B T\lambda_0}\Delta\kappa$, we have

$$\begin{aligned}S(\vec{r}) &= C[\nabla\delta\psi(\vec{r}) - \vec{E}_0]^2 + \delta\mu\frac{\Omega q_0^3}{\lambda_0} \\ &= C[\nabla(\sum_{\vec{G}}\delta\psi(\vec{G})e^{i\vec{G}\cdot\vec{r}}) - \vec{E}_0]^2 + \delta\mu\frac{\Omega q_0^3}{\lambda_0} \\ &= C[\sum_{\vec{G}}\delta\psi(\vec{G})i\vec{G}e^{i\vec{G}\cdot\vec{r}}) - \vec{E}_0]^2 + \delta\mu\frac{\Omega q_0^3}{\lambda_0} \\ &= C[-\sum_{\vec{G}}\sum_{\vec{G}'}(\vec{G}-\vec{G}')\cdot\vec{G}'\delta\psi(\vec{G}-\vec{G}')\delta\psi(\vec{G}')e^{i\vec{G}\cdot\vec{r}} + \vec{E}_0^{\,2} - 2\sum_{\vec{G}}\vec{E}_0\cdot i\vec{G}\delta\psi(\vec{G})e^{i\vec{G}\cdot\vec{r}}] \\ &\quad +\delta\mu\frac{\Omega q_0^3}{\lambda_0}\end{aligned}$$

$$
\begin{aligned}
&= C\vec{E}_0^{\,2} + \delta\mu\frac{\Omega q_0^3}{\lambda_0} - C[\sum_{\vec{G}}(\sum_{\vec{G}'}(\vec{G}-\vec{G}')\cdot\vec{G}'\delta\psi(\vec{G}-\vec{G}')\delta\psi(\vec{G}') - 2\vec{E}_0\cdot i\vec{G}\delta\psi(\vec{G})]e^{i\vec{G}\cdot\vec{r}} \\
&= \sum_{\vec{G}} S(\vec{G})e^{i\vec{G}\,\vec{r}}. \qquad (3.24)
\end{aligned}
$$

The coefficient $S(\vec{G})$ can be computed

$$
\begin{aligned}
S(\vec{G}_0) &= C\vec{E}_0^{\,2} + \delta\mu\frac{\Omega q_0^3}{\lambda_0}, && (3.25) \\
S(\vec{G}_1) &= C[\delta\psi(\vec{G}_{10})\delta\psi(\vec{G}_5) + \delta\psi(\vec{G}_8)\delta\psi(\vec{G}_9)] + C\frac{2i}{B}[\delta\psi(\vec{G}_1)]^2, && (3.26) \\
S(\vec{G}_2) &= C[\delta\psi(\vec{G}_8)\delta\psi(\vec{G}_{12}) + \delta\psi(\vec{G}_5)\delta\psi(\vec{G}_{11})] + C\frac{2i}{B}[\delta\psi(\vec{G}_2)]^2. && (3.27)
\end{aligned}
$$

The other ten $S(\vec{G}_i)$ are of the same form as $S(\vec{G}_1)$ and $S(\vec{G}_2)$

$$
S(\vec{G}_i) = C[\delta\psi(\vec{G}_n)\delta\psi(\vec{G}_l) + \delta\psi(\vec{G}_k)\delta\psi(\vec{G}_m)] + C\frac{2i}{B}[\delta\psi(\vec{G}_i)]^2, \qquad (3.28)
$$

with the same (n, k, m , l) as given in Table 3.1.

So far, we have obtained both $\hat{C}(\vec{G},\vec{G}')$ and $S(\vec{G})$. By solving the matrix equation (2.47), we can get the thirteen $\delta\phi(\vec{G})$ in terms of $\vec{E}$ and $\delta\mu\frac{\Omega q_0^3}{\lambda_0}$. Furthermore, as the incompressible condition equation (2.37) is $\delta\phi(\vec{G}_0) = 0$ in Fourier space. This condition can be used to obtain the term with the Lagrange multiplier $\delta\mu\frac{\Omega q_0^3}{\lambda_0}$, leading to a solution of the twelve $\delta\phi(\vec{G}_i)$'s for $\vec{G}_i$ in the first shell ($|\vec{G}_i| = 1$).

Using the method described above, the structure change of BCC phase under electric filed is examined in the following part. We use the same diblock copolymer as the one has been examined by the single-mode approximation with symmetry assumption [27], with the parameters specified as

$$
f = 0.3, \qquad \chi N = 14.4,
$$

$$
\kappa_A = 6.0, \qquad \kappa_B = 2.5.
$$

The values of the chosen f and χN ensure that the BCC phase is the stable phase at $\vec{E} = 0$. The values of the coefficients in the Landau-Brazovskii free energy corresponding to the above values can be obtained according to the analysis in [30], [31]. we have

$$\xi = 0.1328645, \qquad \tau = 0.0009415, \qquad \gamma = 0.1108282.$$

Using the values ξ, τ and γ, A_1, B and $V(\vec{G})$'s are calculated as

$$\begin{aligned}
A_1 &= 0.0845671, \qquad B = 0.0234994i, \\
V_0 &= 0.0035758, \qquad V_1 = -0.0015137, \\
V_2 &= 0.0011919, \qquad V_3 = 0.0005959, \\
V_4 &= 0.0002979.
\end{aligned}$$

By using the above values and using the electric field in unit of $C^{\frac{1}{2}}$

$$\hat{E}_0 = C^{\frac{1}{2}}\vec{E}_0, \tag{3.29}$$

applying the electric field along the direction (1, 1, 0), we get the values of the twelve $\delta\phi((\vec{G}_i)$ in terms of $\hat{E}_0$,

$$\begin{aligned}
\delta\phi(\vec{G}_1) &= \delta\phi(\vec{G}_3) = -15.0576263\hat{E}_0^{\ 2}, \\
\delta\phi(\vec{G}_2) &= \delta\phi(\vec{G}_4) = 4.5053284\hat{E}_0^{\ 2}, \\
\delta\phi(\vec{G}_5) &= \delta\phi(\vec{G}_6) = \delta\phi(\vec{G}_7) = \delta\phi(\vec{G}_8) = \delta\phi(\vec{G}_9) = \delta\phi(\vec{G}_{10}) = \delta\phi(\vec{G}_{11}) = \delta\phi(\vec{G}_{12}) \\
&= -3.9448313\hat{E}_0^{\ 2}.
\end{aligned}$$

It can be seen that

$$\delta\phi(\vec{G}_1) = \delta\phi(\vec{G}_3) < 0, \qquad \vec{G}_1, \vec{G}_3 // \vec{E}_0,$$

$$\delta\phi(\vec{G}_2) = \delta\phi(\vec{G}_4) > 0, \qquad \vec{G}_2, \vec{G}_4 \perp \vec{E}_0,$$

$$\delta\phi(\vec{G}_5) = \delta\phi(\vec{G}_6) = \delta\phi(\vec{G}_7) = \delta\phi(\vec{G}_8) = \delta\phi(\vec{G}_9) = \delta\phi(\vec{G}_{10}) = \delta\phi(\vec{G}_{11}) = \delta\phi(\vec{G}_{12}) < 0$$

$\vec{G_5}, \vec{G_6}, \vec{G_7}, \vec{G_8}, \vec{G_9}, \vec{G_{10}}, \vec{G_{11}}, \vec{G_{12}}$have equal and non-zero projections on the (1,1,0) axis.

So we can see that when the electric field is zero, all the Fourier coefficients are of the same value, as the electric field increase, the Fourier coefficients corresponding to reciprocal vectors orthogonal to the electric field increase while the Fourier coefficients corresponding to the reciprocal vectors parallel to or have non-zero projections on the electric field direction decrease. Also, the Fourier coefficients corresponding to the reciprocal vectors which are symmetric to the electric field are changed by the same value. Starting at BCC at zero field, the spheres elongate in the direction of the field more and more as the electric field increase. The resulting distorted BCC structure has $I4/mmm$ symmetry.

Now we consider the same situation as has been examined in the single-mode approximation with symmetry assumption in which the electric field is applied along (1, 1, 1) direction. the resulting twelve $\delta\phi(\vec{G_i})$ in terms of $\hat{E}_0$ for the first set of basis vectors are

$$\begin{aligned}
\delta\phi(\vec{G_1}) &= \delta\phi(\vec{G_3}) = \delta\phi(\vec{G_5}) = \delta\phi(\vec{G_7}) = \delta\phi(\vec{G_9}) = \delta\phi(\vec{G_{11}}) \\
&= -10.9095887\hat{E_0}^2, \qquad (3.30) \\
\delta\phi(\vec{G_2}) &= \delta\phi(\vec{G_4}) = \delta\phi(\vec{G_6}) = \delta\phi(\vec{G_8}) = \delta\phi(\vec{G_{10}}) = \delta\phi(\vec{G_{12}}) \\
&= 2.1323810\hat{E_0}^2. \qquad (3.31)
\end{aligned}$$

Here, $\vec{G_2}, \vec{G_4}, \vec{G_6}, \vec{G_8}, \vec{G_{10}}, \vec{G_{12}} \perp \vec{E_0}$, and $\vec{G_1}, \vec{G_3}, \vec{G_5}, \vec{G_7}, \vec{G_9}, \vec{G_{11}}$have equal and non-zero projections on the (1, 1, 1) axis. This result shows that when the electric field is applied, the Fourier coefficients corresponding to the reciprocal vectors which are orthogonal and symmetric to the (1, 1, 1) axis are increased by the same value, while the Fourier coefficients corresponding to the reciprocal vectors which are symmetric to and have equal and nonzero projections on the (1, 1, 1) direction are decreased by the same value. This indicate a structure change. Also, the change of Fourier coefficients which is getting smaller is much larger than the change of the Fourier coefficients which is getting larger. The spheres deformed into ellipsoids with long axis in the (1, 1, 1) direction . The resulting distorted BCC structure has $R\bar{3}m$ symmetry. This is consistent with the result of the SCFT real space calculation. Although, as the electric field is taken as a perturbation in our method, it is only effective for small magnitude of electric filed. The perturbation theory predicts that the structure change of a BCC phase is through the intermediate $R\bar{3}m$ structure when the electric field is along the (1, 1, 1) direction. This prediction confirms the pathway conjectured by Lin et al [18]

Chapter 4

Conclusion

In conclusion, we have developed a method for predicting structural change of diblock copolymers in a weak external electric field. First, we developed a general theory to predict structural change by a linear response calculation in Fourier space. The result shows that an external field will lead to a change in the Fourier components and may lead to new reciprocal lattice vectros. When we applied this theory to the Landau-Brazovakii model for diblock copolymers by taking the electric field as a perturbation, we found that the structural change is an epitaxial change. The result we obtained can be used to predict the structural change of any diblock copolymer ordered phases under electric field. Finally, we studied the structural change of a BCC phase as an example. We used the first mode to describe the order parameter. It is found that only the Fourier coefficients of the order parameter will change, while the basis vectors in the reciprocal space are kept the same. So the resulting structure still maintain some symmetry of the original structure. They are related to each other epitaxially. We demonstrated that the spheres will elongate in the direction of the electric field. In the case the electric field is applied in the (1, 1, 1) direction, the resulting distorted BCC structure has a $R\bar{3}m$ symmetry. This result is consistent with the symmetry assumed by previous researchers and the result obtained from the real-space SCFT method. In the case the electric field is applied in the (1, 1, 0) direction, the resulting distorted BCC structure has a $I4/mmm$ symmetry. In both cases, we obtained the result that the Fourier coefficients corresponding to the reciprocal vectors which are orthogonal to the electric field direction are increased by the same value, and the Fourier coefficients corresponding to the reciprocal vectors which have equal and nonzero projections on the electric field direction are decreased by the same value. This result shows that the structure change follows certain pathways. Although structural change can be studied using real-space numerical methods, our theory provides a simple and analytic method to predict the structural transitions when an external field is applied. Furthermore, the current theory is useful to obtain insight into the symmetry changes with the applied field. These advantages of the perturbation theory will be useful for future studies on the field-induced phase transitions.

Bibliography

[1] F. S. Bates and G. H. Fredrickson, Physics Today 32 (1999).

[2] P.-G. deGennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, NY, 1979).

[3] F. S. Bates, Science **251**, 898 (1991).

[4] Z. R. W. E. Helfand, Macromolecules **9**, 879 .

[5] L. Leibler, Macromolecules **13**, 1602 (1980).

[6] A. N. Semenov, Sov. Phys. -JETP **61**, 733 (1985).

[7] M. W. Matsen and M. Schick, Phys. Rev. Lett. **72**, 2660 (1994).

[8] M.W.Matsen, J.Phys.: Condens. Matter **14**, R21 (2002).

[9] D. A. Hajduk *et al.*, Macromolecules **27**, 4063 (1994).

[10] L. D. Landau, Phys. Z. Sowjetunion **11**, 545 (1937).

[11] S. A. Brazovskii, Sov. Phys. -JETP **41**, 85 (1975).

[12] I. W. Hamley and V. E. Podneks, JETP Lett **41**, 617 (1996).

[13] M. Park *et al.*, Science **276**, 1401 (1997).

[14] S. Walheim, E. Schaffer, J. Mlynek, and U. Steiner, Science **283**, 520 (1999).

[15] K. Amundson, E. Helfand, X. Quan, and S. D. Smith, Marcromolecules **26**, 2698 (1993).

[16] K. Amundson *et al.*, Marcromolecules **27**, 6559 (1994).

[17] G. G. Pereira and D. R. M. Williams, Macromolecules **32**, 8115 (1999).

[18] C.-Y. Lin, M. Schick, and D. Andelman, Macromolecules **38**, 5766 (2005).

[19] T. Xu *et al.*, Macromolucules **38**, 10788 (2005).

[20] Y. Tsori and D. Andelman, Macromolecules **35**, 5161 (2002).

[21] M. W. Matsen, J. Chem. Phys. **124**, 074906 (2006).

[22] T. Xu *et al.*, Macromolecules **37**, 6980 (2004).

[23] H. Xiang, C.-Y. Lin, and T. P. Russell, Macromolecules **37**, 5358 (2004).

[24] M. W. Matsen., 2005, unpublished.

[25] Y. Tsori, F. Tournilhac, D. Andelman, and L. Leibler, Phys. Rev. Lett **90**, 145504 (2003).

[26] Y. Jiang, H. Liang, and A.-C. Shi, 2006, unpublished.

[27] Y. Tsori, D. Andelman, C.-Y. Lin, and M. Schick, Macromolecules **39**, 289 (2006).

[28] G. H. Fredrickson and E. Helfand, J. Chem. Phys. **87**, 697 (1987).

[29] A.-C. Shi, J. Phys.: Condens. Matter **11**, 10183 (1999).

[30] T. Ohta and K. Kawasaki, Macromolecules **19**, 2621 (1986).

[31] R. A. Wickham, A. C. Shi, and Z. G. Wang, J. Chem. Phys **118**, 10293 (2003).

[32] A. Ranjan and D. C. Morse, Macromolecules (in press 2007).