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Electric Field Effects and Form Birefringence in Diblock Copolymers

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ABSTRACT: We investigate effects of the electric field on diblock copolymers by assuming an induced dipolar interaction among the composition fluctuations. First, we show that, when an electric field is applied perpendicularly to lamellae, undulations start to grow if their in-plane wavenumbers are smaller than an electric wavenumber q_e proportional to the field. Subsequently, the undulations grow into larger spatial structures, eventually leading to a final square-lattice pattern. Second, we calculate the Maxwell stress tensor due to the electric field to predict a finite shear modulus in a lamellar state oriented by the electric field. Third, we examine form birefringence in disordered and ordered phases. In particular, the lamellar and hexagonal phases are shown to become birefringent on spatial scales longer than the spacing of lamellae or cylinders, even if the constituent monomers are optically isotropic. This gives rise to enhancement of depolarized light scattering from lamellar microstructures, which has indeed been observed recently. Most predictions in this paper are applicable to many situations other than those in the electric field.

I. Introduction

Recently, considerable attention has been paid to the effects of the electric field in various fluids in the neighborhood of phase transitions. In particular, diblock copolymers, which are composed of two chemically bonded polymers, are unique systems because they form various mesoscopic structures depending on the temperature T and the volume fraction f of one polymer in a diblock chain.[1–3] Amundson et al.[4] observed that lamellar planes in a diblock copolymer system are orientated in the directions parallel to the electric field, although the alignment is much milder and slower than in shear flow. Their work elucidates a crucial role of defect motion in the alignment process. Block copolymers also exhibit large form birefringence when the composition fluctuations are anisotropic such as in electric field or shear flow.[5,6] Balsara et al. observed enhanced depolarized light scattering from irregularly oriented, lamellar microstructures, whose optical anisotropy is mainly due to the form origin.[7] At this stage of research we aim to study some unexplored aspects of electric field effects in diblock copolymers.

In analyzing their experiment Amundson et al. assumed that the dielectric constant ϵ is a scalar isotopic quantity dependent on the local polymer composition $\phi(\mathbf{r})$. Namely, the anisotropic part of the electric polarizability tensor of the monomers is neglected. Then the electrostatic energy F_E due to the composition fluctuations of lamellar structures was written in terms of the Fourier transformation $\phi_\mathbf{q}$ of $\phi(\mathbf{r})$ as

$$F_E = \frac{1}{2} g_e (2\pi)^{-3} \int d\mathbf{q}\, (\mathbf{e}\cdot\mathbf{q}/q)^2 \phi_\mathbf{q} \phi_{-\mathbf{q}} \tag{1}$$

where $\mathbf{e}$ is the unit vector in the direction of the average field $\bar{\mathbf{E}}$. The coefficient g_e is defined by

$$g_e = (4\pi\bar{\epsilon})^{-1} (\partial\epsilon/\partial\phi)^2 \bar{E}^2 \tag{2}$$

where $\bar{\epsilon}$ is the average dielectric constant and $\bar{E} = |\bar{\mathbf{E}}|$. We will simply use ϵ and $\mathbf{E}$ instead of their spatial averages unless confusion can occur. We notice that inhomogeneities varying in the direction of $\bar{\mathbf{E}}$ increase the electrostatic energy, so lamellar planes should tend to be parallel to the field to lower the free energy. Here we would like to stress that the interaction free energy (1) coincides with an induced dipolar interaction among the composition fluctuations originally derived by Onuki and Doi for nonionic near-critical fluids.[8,9] That is, when $\epsilon(\mathbf{r})$ is weakly inhomogeneous, the deviation $\delta\psi$ of the electric potential satisfies

$$\epsilon \nabla^2 \delta\psi(\mathbf{r}) = \mathbf{E}\cdot\nabla\epsilon(\mathbf{r}) \tag{3}$$

which follows from the equation $\nabla\cdot\epsilon\mathbf{E} = 0$ of electrostatics.[10] The effective charge density is therefore given by $\rho_{\rm eff}(\mathbf{r}) = \mathbf{E}\cdot\nabla\epsilon/4\pi \cong (\partial\epsilon/\partial\phi)\bar{\mathbf{E}}\cdot\nabla\phi/4\pi$. The resultant Coulomb interaction in the bilinear order in the deviation $\delta\phi$ is of the form

$$F_E = (8\pi)^{-1} g_e \int d\mathbf{r} \int d\mathbf{r}'\, (\mathbf{e}\cdot\nabla\phi(\mathbf{r})) \frac{1}{|\mathbf{r}-\mathbf{r}'|} (\mathbf{e}\cdot\nabla'\phi(\mathbf{r}')) \tag{4}$$

which may be rewritten as (1) in the Fourier space. We also note that there is a small shift of the transition temperature due to the electric field.[11–13]

On the other hand, in the disordered phase in the electric field, the system is uniaxial in the direction $\mathbf{e}$ of the field and the mean field structure factor is calculated in the form[1–3]

$$S_\mathbf{q} = \langle|\phi_\mathbf{q}|^2\rangle \cong k_B T/[\bar{r} + D(q-q_0)^2/q_0^2 + g_e(\mathbf{e}\cdot\mathbf{q})^2/q^2] \tag{5}$$

where $\bar{r}$ is the temperature coefficient expressed as

$$\bar{r} = A_0(T - T_c(E)) = A_0(T - T_c(0) - \Delta T_c) \tag{6}$$

where A_0 is a constant and $\Delta T_c = T_c(E) - T_c(0)$ is the shift of the (mean field) transition temperature due to the electric field.[9,11–13] The peak wavenumber q_e is on the order of the inverse gyration radius and D is the coefficient of the gradient term in the free energy density for the composition. The form (5) suggests that, as T is lowered, the fluctuations homogeneous along $\mathbf{e}$ trigger instability at $T = T_c(E)$, while those inhomoge-

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neous along **e** are suppressed by the electric field. Thus, very close to the transition temperature such that

$$g_e \gtrsim |\bar{r}| \tag{7}$$

the dipolar interaction nonlinearly alters the fluctuations at $q \sim q_e$. A similar crossover has also been predicted for near-critical fluids.[9] It is known that the phase transition from a disordered phase to a lamellar phase at the critical composition is weakly first order due to fluctuation effects.[14] The condition (7) at the transition is written as $g_e/\rho_c k_B T > 40/\bar{N}^{1/3}$ in the notation of ref 14, where ρ_c is the chain number density and $\bar{N} = 6^3(R_g{}^3\rho_c)^2$, R_g being the gyration radius. In this strong field condition the discontinuities at the first-order phase transition decrease with increasing g_e.[14]

As a classic effect liquid droplets suspended in another liquid can be deformed and even broken by the intense electric field.[15] Similarly, a planar interface between two immiscible fluids also becomes unstable against long wavelength undulations when an electric field is applied perpendicularly to the interface.[16] In a more complicated situation of phase separation in polymer mixtures, elongation of domains induced by the electric field has also been observed.[17] In the case of nonionic fluids without anisotropy of the dielectric tensor, these effects can be explained within the classical theory of electrostatics. Let us then clarify the relation between the classical theory and our theory. As explicitly shown in ref 16, the classical results in the case $|\epsilon_1 - \epsilon_2| \ll \epsilon_1$ are reproduced from our scheme if we set $\phi(\mathbf{r}) = \epsilon_1$ or ϵ_2 depending on wheter **r** is inside or outside the droplet. This means that we take the thin limit of interface thickness. Here ϵ_1 and ϵ_2 are the dielectric constants inside and outside the droplet, respectively. Then the expression (4) is rewritten in the following surface integral on the interface

$$F_E = (32\pi^2\bar{\epsilon})^{-1}(\epsilon_1 - \epsilon_2)^2\bar{E}^2\int \mathrm{d}a \int \mathrm{d}a' \, (\mathbf{e}\cdot\mathbf{n}_a)\frac{1}{|\mathbf{r}_a - \mathbf{r}_{a'}|}(\mathbf{e}\cdot\mathbf{n}_{a'}) \tag{8}$$

where da and da' are the surface elements at the two interface positions $\mathbf{r}_a$ and $\mathbf{r}_{a'}$, respectively. The **n** and **n**′ are the normal unit vectors. In the case $|\epsilon_1 - \epsilon_2| \ll \epsilon_1$, the interface deformations induced by the electric field may be discussed using the above simplified electrostatic energy (8) and the surface energy. Ohta et al. have recently taken this approach to study the interface motion in phase separation.[18]

In a very different theory Gurovich[19] has examined the effects of chain deformations on the microphase transition due to anisotropy in the electric polarizability tensor

$$\alpha_{ij} = \bar{\alpha}\delta_{ij} + (\Delta\alpha)\left(n_i n_j - \frac{1}{3}\delta_{ij}\right) \tag{9}$$

of monomers in block copolymers. Here the dipolar interaction has been neglected. His calculation of the structure factor in the random phase approximation indicates that, if $|\Delta\alpha|E^2 \ll k_BT$, the additional terms in the free energy density are of the order $\rho_0 N^{-1}(\Delta\alpha)E^2\phi(\mathbf{r})^2$ for the composition fluctuations with wavenumbers on the order of the inverse gyration radius.[19] Here ρ_0 is the monomer number density and N is the polymerization index much larger than 1. Note that the small factor N^{-1} appears in the coefficient. In most polymers we have $|\Delta\alpha| \ll \bar{\alpha}$ and $\epsilon \cong \rho_0\bar{\alpha}$, so that the relative strength of the Gurovich interaction and the induced dipolar interaction turns out to be of the order $(|\Delta\alpha|/\bar{\alpha}N)/[(\partial\epsilon/\partial\phi)/\epsilon]^2$. This ratio is much smaller than 1 in most polymers; namely,

$$|\Delta\alpha|/(\bar{\alpha}N) \ll [(\partial\epsilon/\partial\phi)/\epsilon]^2 \tag{10}$$

Under this condition we may neglect the Gurovich mechanism as in the theory of Amundson et al. On the other hand, the extra small factor N^{-1} does not appear in the so-called intrinsic birefringence to which each monomer contributes nearly independently.[20] Interestingly, the form birefringence arises from anisotropic composition fluctuations and is derivable just from the dipolar interaction (1).[8] Thus, if N is large, the role of the intrinsic contribution is much more diminished in microphase separation phenomena than in electric birefringence.

The organization of this paper is as follows. In section II we will examine the dynamics of undulation instability of lamellae induced by the electric field. In section III the Maxwell stress tensor will be calculated in the electric field. In section IV we will formulate a theory of form birefringence and depolarized light scattering in diblock copolymers to analyze recent experiments. These three parts can be read independently.

II. Undulation Instability of Lamellar Structures

Free Energy of Lamellae. Let us prepare a lamellar structure whose normal is oriented in a particular direction, along which the z axis will be taken. Such a structure may be obtained by application of shear flow to a diblock copolymer system below the transition temperature. We then apply an electric field in the z direction at $t = 0$, which will induce long wavelength lamellar undulations to lower the electrostatic energy. Physically, this lamellar instability has the same origin as that of the instability of a single planar interface between two fluids.[16] Hereafter the lamellar displacement in the z direction will be written as $u(\mathbf{r},t)$ and the time variable t is written explicitly. The composition variation may be expressed approximately as

$$\phi(\mathbf{r},t) = 2A\cos(q_0 z - q_0 u(\mathbf{r},t)) \tag{11}$$

where A is the lamellar amplitude dependent on the temperature and the modulation wavenumber q_0 is of the order of the inverse gyration radius slightly below the transition. The displacement $u(\mathbf{r},t)$ is assumed to vary on spatial scales much longer than the lamellar spacing $2\pi/q_0$ in all the directions. From general geometrical arguments for lamellar systems,[21] the free energy F_u due to the undulations can be expressed as

$$F_u = \frac{1}{2}\int \mathrm{d}\mathbf{r}\left\{B\left[\frac{\partial u}{\partial z} - \frac{1}{2}\left|\nabla_\perp u\right|^2\right]^2 + K\left|\nabla_\perp{}^2 u\right|^2\right\} \tag{12}$$

where B is the layer compressibility, K is the elastic splay constant, and $\nabla_\perp$ is the in-plane spatial derivative. Using the coefficient D of the gradient term in the free energy, we obtain

$$B = 8q_0{}^2DA^2 \qquad K = 2DA^2 \tag{13}$$

slightly below the transition,[22,23] so the length $\lambda = (K/B)^{1/2}$ is equal to $1/2q_0$.

We then calculate F_E by assuming the form (11). In the integrand of (1) $\mathbf{e}$ is in the z direction and $(\mathbf{e}\cdot\mathbf{q}/q)^2 = (q_z/q)^2 = 1 - (q_\perp/q)^2 \cong 1 - (q_\perp/q_0)^2$ because of $|q_z| \cong q_0 \gg q_\perp$. Here q_z is the wavenumber of $\phi(\mathbf{r},t)$ (and not that of $u(\mathbf{r},t)$) in the z direction and $q_\perp$ is the in-plane wavenumber. We may then rewrite (1) as

$$F_{\mathrm{E}} = \frac{1}{2} g_{\mathrm{e}} \int \mathrm{d}\mathbf{r}\, \phi(\mathbf{r})^2 - \frac{1}{2} g_{\mathrm{e}} q_0^{\,2} \int \mathrm{d}\mathbf{r}\, |\nabla_\perp \phi(\mathbf{r})|^2 \qquad (14)$$

Here the first term does not depend on u and is not important for the variations of u, while substitution of (11) into the second term yields a negative contribution indicating instability. Namely,

$$F_{\mathrm{E}} = g_e A^2 V - g_e A^2 \int \mathrm{d}\mathbf{r}\, |\nabla_\perp u(\mathbf{r})|^2 \qquad (15)$$

where V is the system volume.

Now up to the bilinear order $F = F_u + F_E$ may be expressed in the form

$$F \cong \frac{1}{2} (2\pi)^{-3} \int \mathrm{d}\mathbf{q}\, C_{\mathbf{q}} |u_{\mathbf{q}}|^2 \qquad (16)$$

where the coefficient $C_{\mathbf{q}}$ is written as

$$C_{\mathbf{q}} = B[q_z^{\,2} + \lambda^2 q_\perp^{\,2}(q_\perp^{\,2} - q_{\mathrm{e}}^{\,2})] \qquad (17)$$

The wavenumber q_e is determined by the external field as

$$q_{\mathrm{e}} = (2g_e/K)^{1/2} A = (g_e/D)^{1/2} \qquad (18)$$

Amundson et al. introduced an electric length, ξ in (4.13) of ref 4c, which is just the inverse of q_e in our theory. For their system it was 500 nm, being about 23 lamellar periods, at E = 18 kV/cm. In the early stage after application of the field, (17) indicates that the undulations grow exponentially if

$$q_z^{\,2}/q_\perp^{\,2} + \lambda^2 q_\perp^{\,2} < \lambda^2 q_{\mathrm{e}}^{\,2} \qquad (19)$$

If $u = 0$ at the upper and lower plates $z = 0$ and d, the minimum wavenumber in the z direction is π/d and the left hand side of (19) is minimized at $q_\perp = (\pi/d\lambda)^{1/2}$. The criterion of the linear instability is thus given by[21]

$$q_{\mathrm{e}}^{\,2} = 2g_e A^2/K > 2\pi/d\lambda \qquad (20)$$

The same type of lamellar instability is well-known in smectic and cholesteric liquid crystals as the Helfrich–Hurault instability under magnetic field or uniaxial tension.[21] Very recently, this instability has also been predicted in diblock copolymers under uniaxial tension.[24,25] In this instability the final surface pattern is a square-lattice wave structure crucially dependent on the sample thickness d in the z direction.[26,27] Namely, the final wavenumbers in the z direction and on the lamellar are

$$q_{z\mathrm{f}} = \pi/d \qquad q_{\perp\mathrm{f}} = (q_{z\mathrm{f}}/\lambda)^{1/2} = (\pi/d\lambda)^{1/2} \qquad (21)$$

These wavenumbers are just those which minimize the left hand side of (19). If the field is slightly above the critical value determined from (20), $q_{\perp f}$ is of the same order as q_e. However, there should be a coarsening process after application of a field when d is not small such that $q_{\perp f} \ll q_e$ or

$$q_{\mathrm{e}}^{\,2} \gg \pi/d\lambda \qquad (22)$$

This coarsening process has not been examined in the literature, so we will present its numerical analysis in another paper.[28] In the following subsection we will give simple intuitive arguments on this process. However, we will neglect a possible role of defects, although they may be important, as suggested by ref 4.

Dynamics of Undulation Instability. We here propose dynamic equations of u and the velocity field $\mathbf{v}(\mathbf{r},t)$, which may be derived from the time-dependent Ginzburg–Landau model of diblock copolymers,[29–31]

$$\frac{\partial}{\partial t} u = \mathbf{v}\cdot(\mathbf{e}_z - \nabla u) - (\Lambda_0 D/K) \frac{\delta(F_{\mathrm{u}} + F_{\mathrm{E}})}{\delta u} \qquad (23)$$

$$\rho \frac{\partial}{\partial t} \mathbf{v} = -\nabla p - \frac{\delta(F_{\mathrm{u}} + F_{\mathrm{E}})}{\delta u} (\mathbf{e}_z - \nabla u) + \eta_0 \nabla^2 \mathbf{v} \qquad (24)$$

where $\mathbf{e}_z$ is the unit vector along the z axis, Λ_0 is the kinetic coefficient in the evolution equation of the composition fluctuations, ρ is the mass density, and η_0 is the background viscosity. The pressure p in (24) is introduced to ensure the incompressibility condition $\nabla\cdot\mathbf{v} = 0$. Notice that the same dynamic equations are well established for smectic liquid crystals.[24] Because the time scale of $\mathbf{v}$ is much faster than that of u, we may set $\rho\partial\mathbf{v}/\partial t = 0$ in (24). In the linear order the Fourier component $u_{\mathbf{q}}$ then obeys

$$\frac{\partial}{\partial t} u_{\mathbf{q}} = -\Gamma_{\mathbf{q}} u_{\mathbf{q}} \qquad (25)$$

with

$$\Gamma_{\mathbf{q}} = L_{\mathbf{q}}[B q_z^{\,2} + K q_\perp^{\,2}(q_\perp^{\,2} - q_{\mathrm{e}}^{\,2})] \qquad (26)$$

We can see that $\Gamma_{\mathbf{q}}$ is negative at small q_z and $q_\perp$. The growth rate $|\Gamma_{\mathbf{q}}|$ of the fluctuations is maximum for $q_z \cong 0$ and $q_\perp \sim q_e$. Due to the hydrodynamic interaction the coefficient $L_{\mathbf{q}}$ behaves anomalously at small q as[32]

$$L_{\mathbf{q}} = \frac{\Lambda_0 D}{K} + \frac{q_\perp^{\,2}}{\eta_0 q^4} \qquad (27)$$

Obviously, elimination of $\mathbf{v}$ yields the second term of (27). Comparing the two terms in (27), we obtain a hydrodynamic crossover wavenumber q_h by

$$q_{\mathrm{h}} = (K/\Lambda D \eta_0)^{1/2} = (2/\Lambda \eta_0)^{1/2} A \qquad (28)$$

It is of order A/R_G in the Rouse dynamics and of order AN_e/NR_G in the reptation dynamics (or in the entangled case), where R_G is the gyration radius, being of order $1/q_0$ slightly below the transition, N is the polymerization index, and N_e is the polymerization index between two entanglements in a chain. On the other hand, in usual liquid crystal systems with small molecular weights, q_h is a microscopic wavenumber and the hydrodynamic interaction governs the dynamics of layers.[21]

The exponential growth in the early stage will saturate on the time scale of $1/\Gamma_{\mathbf{q}}$ at $q_\perp \cong q_e$ and $q_z \cong 0$, at which the quartic term in F_u in (12) and the negative bilinear term in F_E in (15) balance, leading to

$$|\nabla_\perp u| \sim \lambda q_e \tag{29}$$

Then coarsening follows. It is important that the quartic term in F_u cannot prevent the coarsening.[28] Let $q_\perp(t)$ and $q_z(t)$ be the characteristic wavenumbers on the lamellae and in the z axis. Eventually, $q_\perp(t)$ becomes much smaller than q_e. On such large spatial scales the sum of the quartic term in F_u and the negative bilinear term in F_E should be minimized to give (29). Because of this minimization, the other terms, which are much smaller than these two terms, can be dominant in the evolution of the structure. This means that the saturation (29) persists in later stages and the characteristic size of u grows as $1/q_\perp(t)$ since $|\nabla_\perp u| \sim |q_\perp(t)u|$. We may derive the growth law by assuming the following order estimation

$$-\frac{\partial}{\partial t} \ln[q_\perp(t)] \sim L_{\mathbf{q}} K q_\perp(t)^4 \tag{30}$$

at $q_\perp \sim q_\perp(t)$ and $q_z \sim q_z(t)$. The right hand side of the above relation represents the unique inverse time scale of the pattern evolution under the saturation (29) and for very small $q_z(t)$ (as given in (34) below). This results in an algebraic decay

$$q_\perp(t) \propto t^{-\alpha} \tag{31}$$

where $\alpha = 1/4$ or $\alpha = 1/2$ without or with the hydrodynamic interaction, as can be shown from (27). More precisely, for $q_e \gtrsim q_\perp(t) \gtrsim q_h$ we have

$$q_\perp(t) \sim (\Lambda_0 D t)^{-1/4} \tag{32}$$

while for $q_h \gtrsim q_\perp(t) \gtrsim q_{\perp f}$ we have

$$q_\perp(t) \sim (\eta_0/Kt)^{1/2} \tag{33}$$

Thus, in the entangled case there will be a crossover from $\alpha = 1/4$ to $\alpha = 1/2$ at $q_\perp(t) = q_h$ because of large viscosity η_0. On the other hand, $q_z(t)$ may be determined from the balance $Bq_z(t)^2 \sim Kq_\perp(t)^4$, so that

$$q_z(t) \sim \lambda q_\perp(t)^2 \propto t^{-2\alpha} \tag{34}$$

The inhomogeneities in the z axis are much weaker than those on the lamellar, as ought to be the case, and their spatial scale ultimately reaches the sample thickness d. The final square-lattice pattern discussed in the literature is then realized. Note also that only the behavior $\alpha = 1/2$ will be observed in low molecular weight systems because q_h is then a microscopic wavenumber.

Instability in the Oblique Field. We have so far assumed that the applied field is initially perpendicular to the planar lamellae. However, it is easy to generalize our theory to the case of the oblique field in which the angle χ between $\mathbf{e}$ and the z axis is arbitrary. Then in (1) we may set $(\mathbf{e}\cdot\mathbf{q}/q)^2 \cong e_z^2 + [2e_ze_xq_zq_x + (e_xq_x)^2 - (e_zq_\perp)^2]/q_0^2$. Some further calculations yield F_E in the form

$$F_E = g_e(Ae_z)^2V + g_eA^2\int d\mathbf{r}\, [(\mathbf{e}\cdot\nabla u(\mathbf{r}))^2 - e_z^2|\nabla u(\mathbf{r})|^2] \tag{35}$$

See the Appendix for more detailed calculations. We can find the criterion of the linear instability by expressing F_E in the bilinear form (16). In the present case $C_{\mathbf{q}}$ reads

$$C_{\mathbf{q}} = Bq_z^2 + Kq_\perp^4 + 2g_eA^2[(\mathbf{e}\cdot\mathbf{q})^2 - e_z^2q^2] \tag{36}$$

We are interested in the wave vector region $q_z \ll q_\perp$, so that we may set $q_z = 0$ in the last term of (36) to obtain

$$C_{\mathbf{q}} \cong Bq_z^2 + K[q_\perp^4 - \cos(2\chi)(q_eq_x)^2 - (\cos\chi)^2(q_eq_y)^2] \tag{37}$$

in terms of q_e and the angle χ. We have assumed that $\mathbf{e}$ is in the xz plane and that $e_z = \cos\chi$, $e_x = \sin\chi$, and $e_y = 0$. As in (26) the relaxation rate of the undulations is expressed as $\Gamma_{\mathbf{q}} = L_{\mathbf{q}}C_{\mathbf{q}}$. Therefore, if $\mathbf{q}$ is in the y direction, the instability occurs under $q_e^2(\cos\chi)^2 > 2\pi/d\lambda$, as can be suggested by (20). However, if $\mathbf{q}$ is in the x direction, the instability is triggered only for $\chi < \pi/4$. We may thus predict that, as $\mathbf{e}$ is inclined from the z axis, the patterns on the lamellae tend to be one-dimensional, varying perpendicularly to $\mathbf{e}$ (or in the y direction). It is of great interest to observe such a crossover from two-dimensional to one-dimensional patterns.

III. Aligned Lamellae and Maxwell Stress

Let us apply an electric field in one of the in-plane directions of an aligned lamellar structure, along which the x axis will be taken. This is the most favorable case, and the lamellar structure is stabilized by the field. The equilibrium correlation function of $u_{\mathbf{q}}$ is given by

$$\langle|u_{\mathbf{q}}|^2\rangle = k_BT/[Bq_z^2 + Kq_\perp^4 + 2A^2g_eq_x^2] \tag{38}$$

On the macroscopic level, the electric field makes the system behave as a solid against small shear deformations in the xz plane in principle. In fact, because tilting of the lamellae by a small angle γ from the x axis increases the electrostatic free energy by $A^2g_e\gamma^2$ per unit volume, the aligned lamellae have a small shear elastic modulus μ given by

$$\mu = 2A^2g_e \tag{39}$$

which is typically of the order of the electrostatic energy density multiplied by A^2 and is extremely small.

We examine in more detail the Maxwell stress tensor due to the electric field when the normal direction $\mathbf{n}$ of the lamellae and the field direction $\mathbf{e}$ are arbitrary. It is well-known that in the absence of electric field the stress due to the composition fluctuations in diblock copolymers may be written in terms of the structure factor $S_{\mathbf{q}}$ as[22,29,30]

$$\sigma_{ij}^0 = -(2\pi)^{-3}\int d\mathbf{q}\, q_iq_j(1 - q_0^2/q^2)S_{\mathbf{q}} \tag{40}$$

Hereafter we are not interested in the scalar part (proportional to the unit tensor) of the stress. On the other hand, the average of the Maxwell stress in electric field is written as[10]

$$\sigma^{(M)}_{ij} = (4\pi)^{-1}\langle\epsilon E_iE_j\rangle - p_1\delta_{ij} \tag{41}$$

where p_1 is a pressure contribution and will be neglected. As discussed in the Introduction, the electric field $\mathbf{E}$ consists of the average $\bar{\mathbf{E}}$ and the inhomogeneous fluctuation $\delta\mathbf{E} = -\nabla\delta\phi$, where $\delta\phi$ is determined from (3). The average Maxwell stress can then be expressed in terms of the structure factor as

$$\sigma^{(\mathrm{M})}{}_{ij} = (4\pi)^{-1}\bar{\epsilon}\bar{E}_i\bar{E}_j - g_{\mathrm{e}}(2\pi)^{-3}\int \mathrm{d}\mathbf{q} \left[\frac{1}{q^2}(\mathbf{q}\cdot\mathbf{e})q_iq_j - q_ie_j - q_je_i\right]\frac{(\mathbf{q}\cdot\mathbf{e})}{q^2}S_{\mathbf{q}} \quad (42)$$

where $\mathbf{e}$ is the unit vector along the average field, so $\bar{E}_i = \bar{E}e_i$. In the lamellar phase $S_{\mathbf{q}}$ is peaked at $q = q_0$; hence, the wave vector $\mathbf{q}$ in the above integrand may be replaced by $q_0\mathbf{n}$, where $\mathbf{n}$ is the lamellar normal. This approximation yields a simpler formula

$$\sigma^{(\mathrm{M})}{}_{ij} = (4\pi)^{-1}\bar{\epsilon}\bar{E}_i\bar{E}_j - g_{\mathrm{e}}\langle\phi^2\rangle[(\mathbf{n}\cdot\mathbf{e})n_in_j - n_ie_j - n_je_i](\mathbf{n}\cdot\mathbf{e}) \quad (43)$$

where $\langle\phi^2\rangle = (2\pi)^{-3}\int\mathrm{d}\mathbf{q}\ S_{\mathbf{q}}$ is the average of $\phi(\mathbf{r})^2$ at one spatial point and is equal to $2A^2$ if (11) is assumed. If the angle χ between $\mathbf{n}$ and $\mathbf{e}$ is close to $\pi/2$, the second term of (43) gives rise to a shear stress, $\mu\cos\chi$, with $\mu = k_{\mathrm{B}}Tg\langle\phi^2\rangle$ in accord with (39) under (11).

The aligned lamellae have a very small yield stress against shear deformations and are very fragile solids, so they can be easily broken by applied shear. It now seems interesting to investigate how orientation due to the electric field and that due to weak shear flow compete in lamellar phases.

IV. Form Birefringence and Depolarized Scattering

We examine the form part of birefringence and depolarized light scattering from diblock copolymer systems by extending the theory in ref 33. We assume that the local optical dielectric tensor is isotropic but weakly inhomogeneous as $\epsilon_o(\mathbf{r}) = \bar{\epsilon}_o + \delta\epsilon_o(\mathbf{r})$, neglecting the intrinsic anisotropy ($\Delta\alpha = 0$ in (9)). Hereafter the time dependence of $\delta\epsilon_o(\mathbf{r})$ will be suppressed because it is negligibly slow as compared to that of the electric field. The subscript o of the dielectric constant denotes taking the value at the optical frequencies, and the average $\bar{\epsilon}_o$ will be simply written as ϵ_o unless confusion may occur. The electric field inside the medium obeys

$$\left(\nabla^2\overleftrightarrow{I} - \nabla\nabla\cdot\right)\mathbf{E}(\mathbf{r},t) = -\frac{1}{c^2}\frac{\partial^2}{\partial t^2}[\epsilon_o(\mathbf{r})\mathbf{E}(\mathbf{r},t)] \quad (44)$$

where $\overleftrightarrow{I}$ is the unit tensor. We expand the electric field in powers of the deviation $\delta\epsilon_o(\mathbf{r})$ as

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0(\mathbf{r},t) + \mathbf{E}_1(\mathbf{r},t) + \mathbf{E}_2(\mathbf{r},t) + \ldots \quad (45)$$

The first term $\mathbf{E}_0(\mathbf{r},t) = E_0\cos(kx - \omega_0t)\mathbf{e}_i$ represents the unperturbed field, where $k = \epsilon_o^{1/2}\omega_0/c$ and $\mathbf{e}_i$ is the unit vector along the initial polarization. The Fourier transformation of the first correction $\mathbf{E}_1(\mathbf{r},t)$ in space and time may be solved in the form

$$\mathbf{E}_{1\mathbf{q}\omega} = \frac{-\mathbf{q}\mathbf{q} + k^2\overleftrightarrow{I}}{q^2 - k^2 - i0}\frac{1}{\epsilon_o}(\delta\epsilon_o\mathbf{E}_0)_{\mathbf{q}\omega} \quad (46)$$

We then perform the inverse-Fourier transformation of the above equation using the retarded Green function to obtain $\mathbf{E}_1(\mathbf{r},t)$ in the real space.[33] Note that $-i0$ in the denominator is a positive infinitesimal number arising from the causality law. As is well-known, $\mathbf{E}_1(\mathbf{r},t)$ far from the scattering region is obtained in the form[34]

$$\mathbf{E}_1(\mathbf{r},t) = \left(\frac{k^2E_0}{4\pi\epsilon_o}\right)\frac{1}{r}\mathrm{Re}\left[\int\mathrm{d}\mathbf{r}'\ \delta\epsilon_o(\mathbf{r}')\exp(i\mathbf{q}_{\mathrm{s}}\cdot\mathbf{r}' + ikr - i\omega_0t)\right]\mathbf{e}_i \quad (47)$$

where $\mathbf{q}_{\mathrm{s}} = \mathbf{k} - (k/r)\mathbf{r}$ is the scattering wave vector and the integration is within the scattering region. On the other hand, inside the scattering region we simply obtain

$$\mathbf{E}_{1\mathbf{q}\omega} \cong -q^{-2}\mathbf{q}\mathbf{q}\frac{1}{\epsilon_o}(\delta\epsilon_o\mathbf{E}_0)_{\mathbf{q}\omega} \quad (48)$$

because $k \ll q_0$. Namely, the laser beam is almost homogeneous on the spatial scale of $\delta\epsilon_o(\mathbf{r})$ in diblock copolymers. Furthermore, we replace the first factor q^{-2} in the above equation by q_0^{-2} to obtain a local form in the real space

$$\mathbf{E}_1(\mathbf{r},t) \cong q_0^{-2}\nabla\nabla\left[\frac{1}{\epsilon_o}\delta\epsilon_o(\mathbf{r})\mathbf{E}_0(\mathbf{r},t)\right] \quad (49)$$

The form part $\overleftrightarrow{\epsilon}_{\mathrm{f}}$ of the effective dielectric tensor inside the medium is defined by[33]

$$\langle\mathbf{D}\rangle = \langle\epsilon_o(\mathbf{r})\mathbf{E}(\mathbf{r},t)\rangle = (\epsilon_o\overleftrightarrow{I} + \overleftrightarrow{\epsilon}_{\mathrm{f}})\langle\mathbf{E}\rangle \quad (50)$$

Then we obtain $\overleftrightarrow{\epsilon}_{\mathrm{f}}$ on the second order of $\delta\epsilon_o$ in the form

$$\overleftrightarrow{\epsilon}_{\mathrm{f}}\mathbf{E}_0 = \langle\delta\epsilon_o(\mathbf{r})\mathbf{E}_1(\mathbf{r},t)\rangle \quad (51)$$

If use is made of (48), we may express the ij component of the form part in terms of the structure factor $S(\mathbf{q})$ as

$$\epsilon_{\mathrm{f}ij} = -[(\partial\epsilon_o/\partial\phi)^2/\epsilon_o](2\pi)^{-3}\int\mathrm{d}\mathbf{q}\ (q_iq_j/q^2)S(\mathbf{q}) \quad (52)$$

Further use of (49) yields a very simple expression in the real space representation

$$\epsilon_{\mathrm{f}ij} = -[(\partial\epsilon_o/\partial\phi)^2/\epsilon_oq_0^{\,2}]\left\langle\frac{\partial\phi(\mathbf{r})}{\partial x_i}\frac{\partial\phi(\mathbf{r})}{\partial x_j}\right\rangle \quad (53)$$

The average $\langle\ldots\rangle$ here is taken over the composition fluctuations. Note that the above simple expression (53) can be used even in nonstationary states and in both disordered and ordered phases.

So far we have neglected the imaginary part of the form dielectric tensor, which represents anisotropy of scattering and is known as form dichroism.[33,36,37] It can be significant only when the spatial scale of scattering objects is comparable to or longer than the laser light wavelength, so it is small in diblock copolymers with $q_0 \gg k$. It is worth noting that in usual binary mixtures both birefringence and dichroism grow near the consolute critical point irrespectively of their molecular weights.[33,36,37]

Disordered Phase. Particularly in the disordered phase in the electric field in the direction $\mathbf{e}$, the structure factor is given by (5). The form dielectric tensor may then be expressed as

$$\epsilon_{\mathrm{f}ij} = \epsilon_{\mathrm{df}}\delta_{ij} + (\Delta\epsilon_{\mathrm{df}})\left(e_ie_j - \frac{1}{3}\delta_{ij}\right) \quad (54)$$

The anisotropic part $\Delta\epsilon_{\rm df}$ may be calculated to first order in $g_{\rm e}$ or E^2 as

$$\Delta\epsilon_{\rm df}/\epsilon_{\rm o} = (60\pi)^{-1}[(\partial\epsilon_{\rm o}/\partial\phi)/\epsilon_{\rm o}]^2 q_0{}^2 g_{\rm e}/(D^{1/2}\bar{r}^{3/2}) \quad (55)$$

Interestingly, $\Delta\epsilon_{\rm df}$ grows as $\bar{r}^{-3/2}$ at small $\bar{r}$, which is very analogous to the behavior of the zero-frequency shear viscosity[29,30] and that of flow birefringence[30,35] in the disordered phase near the microphase transition.

We also calculate the transient electric birefringence (the Kerr effect)[9,38] after an electric field has been switched off at $t = 0$. In this relaxation the structure factor $S_{\mathbf{q}}(t) = \langle|\phi_{\mathbf{q}}(t)|^2\rangle$ is assumed to relax in time as[8]

$$S(\mathbf{q},t) \cong S_q{}^{(0)} - (g_{\rm e}/k_{\rm B}T)(\mathbf{q}\cdot\mathbf{e}/q)^2[S_q{}^{(0)}]^2 \exp(-2\gamma_q t) \quad (56)$$

where $S_q{}^{(0)}$ is the equilibrium structure factor without the electric field ($g_{\rm e} = 0$ in (5)) and γ_q is the relaxation rate dependent on q. Then the anisotropy of the optical dielectric tensor decays from the stationary value (54) to zero as

$$\Delta\epsilon_{\rm df}(t) \cong (\Delta\epsilon_{\rm df}) \exp(-2\gamma_0 t) \quad (57)$$

where γ_q in (56) has been replaced by its value γ_0 at the peak $q = q_0$. The relaxation rate $2\gamma_0$ can be slow near the transition, while the relaxation of the intrinsic part occurs on faster time scales. As another experimental method Hoffmann and Krämer[39] have measured electric birefringence under an alternating field (dynamic electric birefringence) in micellar and colloidal solutions and polyelectrolyte solutions. It can be a powerful method also in block copolymers.

Ordered Phase. In the lamellar phase simple and interesting results can be obtained. We assume that the lamellar normal $\mathbf{n}(\mathbf{r})$ changes slowly in space compared to the lamellar spacing $2\pi/q_0$ and that the variation of the lamellar spacing is negligibly small. From (11) and (49) the first-order correction $\mathbf{E}_1$ of the electric field is written as

$$\mathbf{E}_1(\mathbf{r},t) \cong -\frac{1}{\epsilon_{\rm o}}\delta\epsilon_{\rm o}(\mathbf{r})\mathbf{E}_0(\mathbf{r},t)\cdot\mathbf{n}(\mathbf{r})\mathbf{n}(\mathbf{r}) \quad (58)$$

The form part of the dielectric tensor is then given by

$$\epsilon_{{\rm f}ij} = -2[(\partial\epsilon_{\rm o}/\partial\phi)^2/\epsilon_{\rm o}]A^2\langle n_i(\mathbf{r})n_j(\mathbf{r})\rangle \quad (59)$$

where A is the lamellar amplitude appearing in (11). Reference 6 has already presented essentially the same formula.

Note that the above formula is obtained by averaging over the fluctuations on the scale of the lamellar spacing $2\pi/q_0$. Therefore, if we are interested in electromagnetic fields with wavelengths much longer than $2\pi/q_0$, the lamellae phase may be regarded to be optically anisotropic characterized by the following local, anisotropic dielectric tensor

$$\overleftrightarrow{\epsilon}_{\rm o} = \bar{\epsilon}_{\rm o}\overleftrightarrow{I} + (\Delta\epsilon_{\rm o})\mathbf{nn} \quad (60)$$

with

$$\Delta\epsilon_{\rm o} = -\frac{2}{\epsilon_{\rm o}}\left(\frac{\partial\epsilon_{\rm o}}{\partial\phi}\right)^2 A^2 < 0 \quad (61)$$

In other words, the lamellar phase of diblock copolymers is optically birefringent on spatial scales longer than the lamellar spacing even if the constituent monomers are optically isotropic.

Also for other ordered structures we may readily calculate the effective dielectric tensor similar to (60). Let us consider hexagonally packed cylinders aligned along the z axis. Slightly below the transition from the disordered phase, the order parameter ϕ may be expressed as[1-3]

$$\phi(\mathbf{r}) = 2A_{\rm h}[\cos(q_0\mathbf{e}_1\cdot\mathbf{r}) + \cos(q_0\mathbf{e}_2\cdot\mathbf{r}) + \cos(q_0\mathbf{e}_3\cdot\mathbf{r})] \quad (62)$$

where the three unit vectors $\mathbf{e}_1$, $\mathbf{e}_2$, and $\mathbf{e}_3$ are on the xy plane making angles of $\pm 2\pi/3$ between them. Then we obtain

$$\overleftrightarrow{\epsilon}_{\rm o} = \bar{\epsilon}_{\rm o}\overleftrightarrow{I} - \frac{2}{\epsilon_{\rm o}}\left(\frac{\partial\epsilon_{\rm o}}{\partial\phi}\right)^2 A_{\rm h}{}^2[\mathbf{e}_1\mathbf{e}_1 + \mathbf{e}_2\mathbf{e}_2 + \mathbf{e}_3\mathbf{e}_3] \quad (63)$$

Interestingly, the hexagonal phase is birefringent with $\Delta n/n = 2(\partial\epsilon_{\rm o}/\partial\phi)^2 A_{\rm h}{}^2/\epsilon_{\rm o}{}^2$ even when light propagates in the direction of the cylinders.

Depolarized Light Scattering. Balsara et al.[7] have observed a remarkable increase of depolarized light scattering with the appearance of irregularly oriented lamellar grains even when the configuration of the grains are isotropic on the larger scale, statistical average. They have explained this effect by starting with the local anisotropic form (60) of the dielectric tensor. Our theory provides the basis of (60).

As is evident in (47), the scattered light in our case is not depolarized to first order in $\delta\epsilon_{\rm o}$ (because of the assumption $\Delta\alpha = 0$). However, the second-order contribution $\mathbf{E}_2$ is depolarized. In fact, its Fourier transformation is obtained if $\delta\epsilon_{\rm o}\mathbf{E}_0$ on the right hand side of (46) is replaced by $\delta\epsilon_{\rm o}\mathbf{E}_1 - \langle\delta\epsilon_{\rm o}\mathbf{E}_1\rangle$. From (58) we obtain

$$\begin{aligned}\delta\epsilon_{\rm o}\mathbf{E}_1 &= -\epsilon_{\rm o}{}^{-1}(\delta\epsilon_{\rm o})^2\mathbf{E}_0\cdot\mathbf{nn}\\ &\cong (\Delta\epsilon_{\rm o})\mathbf{E}_0\cdot\mathbf{nn}\end{aligned} \quad (64)$$

The second line is the average of the first line on the scale of the lamellar spacing, $\Delta\epsilon_{\rm o}$ being given by (61). This approximation is allowable if we consider only large scale fluctuations. As ought to be the case, $\mathbf{E}_2$ far from the scattering region is just the scattered light due to the second term of (60). Let $\mathbf{e}_{\rm f}$ be the observed polarization vector perpendicular to $\mathbf{e}_i$. Then, as in (47), $\mathbf{E}_2$ far from the scattering region is expressed as

$$\mathbf{e}_{\rm f}\cdot\mathbf{E}_2(\mathbf{r},t) = (\Delta\epsilon_{\rm o})\left(\frac{k^2E_0}{4\pi\epsilon_{\rm o}}\right)\frac{1}{r}{\rm Re}[\int {\rm d}\mathbf{r}'\ [\mathbf{n}(\mathbf{r}')\cdot\mathbf{e}_i] \times [\mathbf{n}(\mathbf{r}')\cdot\mathbf{e}_{\rm f}] \exp(i\mathbf{q}_{\rm s}\cdot\mathbf{r}' + ikr - i\omega_0 t)] \quad (65)$$

The depolarized scattered light intensity is thus written as

$$I_{\rm d}(\mathbf{q}_{\rm s}) = \langle|\mathbf{e}_{\rm f}\cdot\mathbf{E}_2|^2\rangle = A_{\rm s}|E_0|^2\frac{1}{r^2}\int{\rm d}\mathbf{r}'\int{\rm d}\mathbf{r}''\ C(\mathbf{r}',\mathbf{r}'') \exp(i\mathbf{q}_{\rm s}\cdot(\mathbf{r}' - \mathbf{r}'')) \quad (66)$$

where $A_{\rm s} = {}^1\!/_2((\Delta\epsilon_{\rm o})/4\pi\epsilon_{\rm o})^2k^4$ and $C(\mathbf{r}',\mathbf{r}'')$ is the following correlation function

$$C(\mathbf{r}',\mathbf{r}'') = \langle[\mathbf{n}(\mathbf{r}')\cdot\mathbf{e}_i][\mathbf{n}(\mathbf{r}')\cdot\mathbf{e}_{\rm f}][\mathbf{n}(\mathbf{r}'')\cdot\mathbf{e}_i][\mathbf{n}(\mathbf{r}'')\cdot\mathbf{e}_{\rm f}]\rangle \quad (67)$$

The integrations in (66) are taken within the scattering region. The above expressions are analogous to those of scattered light due to orientation fluctuations in optically anisotropic polymers.[40]

If the orientation distribution of $\mathbf{n}$ is isotropic, $C(\mathbf{r}',\mathbf{r}'')$ depends only on the distance $|\mathbf{r}' - \mathbf{r}''|$ and may be written as $C(|\mathbf{r}'-\mathbf{r}''|)$ with $C(0) = {}^1/_{15}$. Furthermore, it tends to zero if $|\mathbf{r}' - \mathbf{r}''|$ is much longer than the average grain size ℓ_{av}. This is because $\langle[\mathbf{n}(\mathbf{r}')\cdot\mathbf{e}_i][\mathbf{n}(\mathbf{r}')\cdot\mathbf{e}_{\mathrm{f}}]\rangle = {}^1/_3\, \mathbf{e}_i\cdot\mathbf{e}_{\mathrm{f}} = 0$. In this isotropic case Balsara et al. have calculated the depolarized light intensity integrated on the detector plane placed in the forward direction of the laser beam. Its expression is particularly simple when the grain size ℓ_{av} is so long that most of the depolarized light is incident on the detector. Here the typical solid angle of the detector plane seen from the scattering region is of the order of L_{d}/L, L_{d} being the detector dimension and L being the distance between the detector and the scattering region. This condition on ℓ_{av} is expressed as

$$kL_{\mathrm{d}}/L \gg 1/\ell_{\mathrm{av}} \quad \text{or} \quad \ell_{\mathrm{av}} \gg L/kL_{\mathrm{d}} \tag{68}$$

under which we may reproduce a formula of ref 7,

$$\int \mathrm{d}x\, \mathrm{d}y\, I_{\mathrm{d}}(\mathbf{q}_{\mathrm{s}}) \cong \frac{1}{4}(\Delta\epsilon_{\mathrm{o}}/\epsilon_{\mathrm{o}})^2 k^2 E_0^{\,2} V_{\mathrm{s}} \int_0^\infty \mathrm{d}r\, C(r) \tag{69}$$

Here the x and y axes are taken on the detector plane, V_{s} is the scattering volume, and the region of the integration may be pushed to infinity under the condition (68). The last integral in (69) is of the order of ℓ_{av} because $C(r)$ is dimensionless. Note that the above intensity can be measured if the transmitted light is not depolarized (or in the absence of macroscopic birefringence).

V. Summary

(i) We have assumed that the dipolar interaction (1) is the dominant mechanism of field-induced alignment of the composition fluctuations in diblock copolymers as in the theory of Amundson et al.[4] Gurovich's mechanism[19] due to the polarizability anisotropy will not be effective under the condition (10).

(ii) We have found that the electric field induces undulation instability of lamellae at long wavelengths $q_\perp < q_{\mathrm{e}}$, q_{e} being given by (20). The subsequent transient process is very similar to that of spinodal decomposition. In the early stage we expect an exponential growth of the undulations, the growth rate being given by (26). In the late stages the order of magnitude of $|\nabla_\perp u|$, which is the typical angle between the lamellar planes and the field, saturates at $\lambda q_{\mathrm{e}} \sim q_{\mathrm{e}}/q_0$, while the characteristic wavenumbers, $q_\perp(t)$ and $q_z(t)$, parallel and perpendicular to the lamellae decrease in time as (31) and (34). This coarsening process ends when $q_z(t)$ reaches π/d, d being the system thickness. We stress that these predictions are valid also for the instability induced by uniaxial tension.[24,25]

(iii) We have calculated the average Maxwell stress tensor (42) in term of the structure factor. It simply becomes (43) in a lamellar phase, which shows that aligned lamellae have a small elastic shear modulus (39).

(iv) We have examined the form electric birefringence in diblock copolymers to derive general formulas (52) and (53). They lead to (54), (55), and (57) in the disordered phase, (60) and (61) in the lamellar phase, and (63) in the hexagonal phase. The local anisotropic forms (60) and (63) are those obtained on the second order of the inhomogeneous deviation $\delta\epsilon_{\mathrm{o}}$ and may be used on spatial scales longer than the spacing between lamellae or cylinders. The form (60) then readily yields formulas (65), (66), and (69) of depolarized light scattering, which occurs even without intrinsic optical anisotropy and has been observed by Balsara et al.[7]

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Appendix

We calculate the electrostatic energy F_{E} when the angle between the field direction $\mathbf{e}$ and the z axis is arbitrary. Let us introduce $w(\mathbf{r})$ by

$$-\nabla^2 w(\mathbf{r}) = \phi(\mathbf{r}) \tag{A.1}$$

Hereafter the time variable t is suppressed for simplicity. Then F_{E} is expressed as

$$F_{\mathrm{E}} = \frac{1}{2} g_{\mathrm{e}} \int \mathrm{d}\mathbf{r}\, (\mathbf{e}\cdot\nabla\phi)(\mathbf{e}\cdot\nabla w) \tag{A.2}$$

It is convenient to express ϕ and w in terms of complex functions $\Psi(\mathbf{r})$ and $Q(\mathbf{r})$ as

$$\phi(\mathbf{r}) = 2\mathrm{Re}[\Psi(\mathbf{r}) \exp(iq_0 z)] \tag{A.3}$$

$$w(\mathbf{r}) = 2\mathrm{Re}[Q(\mathbf{r}) \exp(iq_0 z)] \tag{A.4}$$

where Ψ and Q change slowly in space as compared to the lamellae spacing $2\pi/q_0$. Re[...] and Im[...] denote taking the real and imaginary part of a complex number. In terms of the lamellar displacement u defined by (11) Ψ is of the form

$$\Psi = A \exp(-iq_0 u) \tag{A.5}$$

From (A.1) Ψ and Q are related by

$$\left[q_0^{\,2} - 2iq_0\frac{\partial}{\partial z} - \nabla^2\right]Q = \Psi \tag{A.6}$$

which is solved to give

$$Q = \left[\frac{1}{q_0^{\,2}} + \frac{2i}{q_0}\frac{\partial}{\partial z} + \frac{1}{q_0^{\,2}}\nabla^2 + \ldots\right]\Psi \tag{A.7}$$

In terms of Ψ and Q, F_{E} may be simply expressed in the form

$$F_{\mathrm{E}} = g_{\mathrm{e}}\mathrm{Re}\left[\int \mathrm{d}\mathbf{r}\, [(\mathbf{e}\cdot\nabla - iq_0 e_z)\Psi^*][(\mathbf{e}\cdot\nabla + iq_0 e_z)Q]\right] \tag{A.8}$$

We substitute (A.7) into (A.8) to obtain

$$F_{\mathrm{E}} \cong e_z^{\,2}\int \mathrm{d}\mathbf{r}\, |\Psi|^2 - (2e_z^{\,2}/q_0)\int \mathrm{d}\mathbf{r}\, \mathrm{Im}\left(\Psi^*\frac{\partial}{\partial z}\Psi\right) + q_0^{-2}\int \mathrm{d}\mathbf{r}\, [|\mathbf{e}\cdot\nabla\Psi|^2 - e_z^{\,2}|\nabla\Psi|^2] \tag{A.9}$$

From (A.5) the second term of (A.9) becomes the space integral of $2e_z^{\,2}A^2\partial u/\partial z$. This term represents the pressure term from the Maxwell stress tensor and is balanced with the pressure from the boundary wall. The first and third terms of (A.9) are now written as in (35).

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