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Solvation and Dissociation in Weakly Ionized Polyelectrolytes<sup>†</sup>

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We present a Ginzburg–Landau theory of inhomogeneous polyelectrolytes with a polar solvent. First, we take into account the molecular (solvation) interaction among the ions, the charged monomers, the uncharged monomers, and the solvent molecules, together with the electrostatic interaction with a composition-dependent dielectric constant. Second, we treat the degree of ionization as a fluctuating variable dependent on the local electric potential. With these two ingredients included, our results are as follows. (i) We derive a mass reaction law and a general expression for the surface tension. (ii) We calculate the structure factor of the composition fluctuations as a function of various parameters of the molecular interactions, which provides a general criterion of the formation of mesophases. (iii) We numerically examine some typical examples of interfaces and mesophase structures, which strongly depend on the molecular interaction parameters.

## I. Introduction

Polyelectrolytes are much more complex than low-molecular-weight electrolytes and neutral polymers.<sup>1–3</sup> Above all, the electrostatic interaction among the ionized monomers on the polymer chains and the mobile ions strongly influences the chain conformations and the mesophase formation.<sup>2–4</sup> Second, the dissociation (or ionization) on the chains should be treated as a chemical reaction in many polyelectrolytes containing weak acidic monomers,<sup>5–7</sup> which is under the influence of the local electric potential. Then, the degree of ionization is a space-dependent annealed variable in inhomogeneous polyelectrolytes, while it has mostly been treated to be a given constant in the theoretical literature. Such ionization heterogeneity should not be negligible in structure formations and in phase separation. Third, for water-like solvents with a large dielectric constant  $\epsilon$ , polymers are often hydrophobic, and small ions are hydrophilic,<sup>6</sup> which can also affect the phase behavior. However, not enough attention has yet been paid on the effects of such short-range molecular interactions, where particularly relevant is the solvation (ion–dipole) interaction between ions and polar molecules.<sup>8</sup>

In this paper, we hence treat the degree of ionization as a fluctuating variable and include the molecular interactions. We show their relevance in polyelectrolytes in the simplest theoretical scheme. That is, we use the so-called random phase approximation<sup>1</sup> in the Flory–Huggins scheme of weakly charged polyelectrolytes.<sup>9–12</sup> On the basis of a recent Ginzburg–Landau theory of ion distributions in binary mixtures,<sup>13–16</sup> we account for the solvation (hydration in aqueous solutions) between the charged particles (ions and ionized monomers) and the solvent molecules, whose free energy contribution usually much exceeds the thermal energy  $T$  (per charged particle).<sup>8</sup> Hereafter, we set the Boltzmann constant equal to unity.

In one-phase states of weakly charged polyelectrolytes, the structure factor  $S(q)$  of the composition fluctuations with wavenumber  $q$  was calculated in the random phase approximation,<sup>9,10</sup> where the solvation interaction was neglected. Let  $\phi$  and  $f$  be the polymer volume fraction and the fraction of charged

monomers on the chains, respectively. In this approximation, the inverse of  $S(q)$  is expressed as

$$\frac{1}{S(q)} = \bar{r}(\phi) + \frac{q^2}{12a\phi(1-\phi)} + \frac{4\pi l_B f^2}{v_0^2(q^2 + \kappa^2)} \quad (1.1)$$

where the first term  $\bar{r}$  depends on  $\phi$  and  $T$ ,  $v_0 = a^3$  is the volume of a monomer,  $l_B = e^2/\epsilon T$  is the Bjerrum length, and  $\kappa$  is the Debye–Hückel wavenumber. Due to the last electrostatic term in eq 1.1,  $S(q)$  can have a peak at an intermediate wavenumber  $q_m$  for small  $\kappa$  or for low salt concentration. We here mention some related experiments. (i) Such a peak has been observed by scattering in one-phase states of charged polymer systems.<sup>17,18</sup> It indicates the formation of mesophases in sufficiently poor solvent, as was confirmed for a semidilute polyelectrolyte solution.<sup>19</sup> (ii) On the other hand, for neutral, polar binary mixtures<sup>13,14</sup> (or a mixture of neutral polymers and a polar solvent)<sup>16</sup> with salt near the critical point, we calculated  $S(q)$  in the same form as in eq 1.1. In electrolytes, the solvation interaction can strongly affect the composition fluctuations, particularly near the critical point. In fact, in a recent scattering experiment,<sup>20</sup> a peak at an intermediate wavenumber has been observed in  $S(q)$  in a near-critical binary mixture with salt. (iii) We also mention a finding of a broad peak in  $S(q)$  in semidilute solutions of neutral polymers in a polar solvent with salt,<sup>21,22</sup> where the solvation effect should be crucial. Thus, we should calculate  $S(q)$  in weakly charged polyelectrolytes including the solvation interaction.

We also mention calculations of the interface profiles in weakly charged polyelectrolytes in a poor solvent using the self-consistent field theory.<sup>23,24</sup> In these papers, however, the solvation interaction was neglected. In polyelectrolytes, the solvation interaction should decisively determine the charge distributions around an interface, as in electrolytes.<sup>14,16</sup> In addition, the degree of ionization should significantly vary across an interface in polyelectrolytes because the dissociation process strongly depends on the local counterion density.

The organization of this paper is as follows. In section II, we will present a Ginzburg–Landau approach accounting for the molecular interactions and the dissociation process. We will

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introduce the grand potential and present a theoretical expression for the surface tension. In section III, we will calculate the composition structure factor generalizing the results in the previous theories.<sup>9,10,13,14</sup> In section IV, we will numerically examine the ion distributions around interfaces and in a periodic state.

## II. Theoretical Background

We suppose weakly charged polymers in a theta or poor solvent consisting of a one-component polar fluid. We assume  $f \ll 1$  to ensure flexibility of the chains. As suggested by Borue and Erukimovich<sup>9</sup> and by Joanny and Leibler,<sup>10</sup> the random phase approximation can be used in concentrated solutions with

$$\phi > f^{2/3}(l_B/a)^{1/3} \quad (2.1)$$

We consider the semidilute case of  $\phi > N^{-1/2}$ , where  $N$  is the polymerization index. Then, the polymers consist of blobs with monomer number  $g = \phi^{-2}$  and length  $\xi_b = ag^{1/2}$  in the scaling theory,<sup>1</sup> and the electrostatic energy within a blob is estimated as

$$\epsilon_b = T(fg)^2 l_B / \xi_b = Tf^2 \phi^{-3} l_B a^{-1} \quad (2.2)$$

Here, the salt density is assumed not to exceed the density of the charged monomers  $n_p$ . Obviously, the condition  $\epsilon_b < T$  yields eq 2.1. In our case, the Debye–Hückel wavenumber  $\kappa \propto (n_p l_B)^{1/2}$  is sufficiently small such that  $n_p \gg \kappa^3$  holds and a free energy contribution due to the charge density fluctuations  $\propto \kappa^3$  is negligible.<sup>25,26</sup>

**A. Ginzburg–Landau Free Energy.** For weakly ionized polyelectrolytes, we set up the free energy accounting for the molecular interactions and the ionization equilibrium. We neglect the image interaction<sup>3,14,27</sup> and the formation of dipole pairs and ion clusters.<sup>12,28</sup> The former is important across an interface when the dielectric constants of the two phases are distinctly different in the dilute limit of the ion densities (see comments in the last section), while the latter comes into play at not small ion densities.

The volume fractions of the polymer and the solvent are written as  $\phi(\mathbf{r})$  and  $1 - \phi(\mathbf{r})$ , respectively. For simplicity, we neglect the volume fractions of the ions and assume that the monomers and the solvent molecules have a common volume  $v_0 = a^3$ . Then,  $\phi$  is also the molar composition. The counterion density is written as  $n_c(\mathbf{r})$ . We may add salt with cation and anion densities of  $n_1(\mathbf{r})$  and  $n_2(\mathbf{r})$ , respectively. The ion charges are  $Z_i$ , with  $i = c, 1$ , and  $2$ . In the monovalent case, for example, we have  $Z_c = 1$ ,  $Z_1 = 1$ , and  $Z_2 = -1$ . In the continuum limit, these variables are smooth ones coarse-grained on the microscopic level.

The number of the ionizable monomers on a chain is  $\nu_M N$ , with  $\nu_M < 1$ . In this work, the degree of ionization  $\zeta(\mathbf{r})$  in the range  $0 \leq \zeta \leq 1$  depends on the surrounding conditions and is inhomogeneous. Then, the fraction of ionized monomers is

$$f = \nu_M \zeta \quad (2.3)$$

and the number density of ionized monomers is

$$n_p = v_0^{-1} f \phi = v_0^{-1} \nu_M \zeta \phi \quad (2.4)$$

where  $\zeta$  and  $\phi$  are space-dependent. The condition of weak ionization  $f \ll 1$  is always satisfied for  $\nu_M \ll 1$ , but we need to require  $\zeta \ll 1$  for  $\nu_M \sim 1$ . Furthermore, we assume that the charge of each ionized group is negative and monovalent (or equal to  $-e$ ) so that the total charge density is written as

$$\rho = e \sum_{i=c,1,2} Z_i n_i - e n_p \quad (2.5)$$

The overall charge neutrality condition is  $\int d\mathbf{r} \rho = 0$ . In more detail in the presence of salt, we have

$$\int d\mathbf{r} [Z_c n_c - n_p] = \int d\mathbf{r} [Z_1 n_1 + Z_2 n_2] = 0 \quad (2.6)$$

The free energy  $F$  of our system is the space integral of a free energy density  $f_T$  in the fluid container. We assume that  $f_T$  is of the form

$$\begin{aligned} f_T = & f_0(\phi, T) + \frac{T}{2} C(\phi) |\nabla \phi|^2 + \frac{\epsilon(\phi)}{8\pi} \mathbf{E}^2 + \\ & T \sum_{i=c,1,2} n_i [\ln(n_i v_0) - 1 + g_i \phi] + T(\Delta_0 + g_p \phi) n_p + \\ & T v_0^{-1} \nu_M \phi [\zeta \ln \zeta + (1 - \zeta) \ln(1 - \zeta)] \end{aligned} \quad (2.7)$$

In the first line, the first term  $f_0$  is the chemical part in the Flory–Huggins form<sup>1,26</sup>

$$f_0 = \frac{T}{v_0 N} \left[ \frac{\phi}{N} \ln \phi + (1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi) \right] \quad (2.8)$$

where  $\chi$  is the interaction parameter dependent on the temperature  $T$  and its critical value is  $\chi_c = (1 + N^{-1/2})^2/2$  in the absence of ions. The second term is the gradient part with the composition-dependent coefficient<sup>1</sup>

$$C(\phi) = 1/12 a \phi(1 - \phi) \quad (2.9)$$

where  $a = v_0^{1/3}$ . The third term is the electrostatic free energy, where  $\mathbf{E} = -\nabla \Phi$  is the electric field. The electrostatic potential  $\Phi$  satisfies the Poisson equation

$$\nabla \cdot \epsilon(\phi) \nabla \Phi = -4\pi \rho \quad (2.10)$$

The dielectric constant  $\epsilon(\phi)$  changes from the solvent value  $\epsilon_0$  to the polymer value  $\epsilon_p$  with increasing  $\phi$ . For simplicity, we assume the linear form

$$\epsilon(\phi) = \epsilon_0 + \epsilon_1 \phi \quad (2.11)$$

where  $\epsilon_1 = \epsilon_p - \epsilon_0$ . In some binary fluid mixtures, the linear form of  $\epsilon(\phi)$  has been measured.<sup>29</sup> For charged gels, Kramarenko et al. pointed out the relevance of the strong composition dependence of  $\epsilon(\phi)$  in the first-order swelling transition.<sup>30</sup> In the second line of eq 2.7, the coupling terms  $T g_i \phi n_i$  ( $i = c, 1, 2, p$ ) arise from the molecular interactions among the charged and uncharged particles, while  $T \Delta_0$  is the dissociation energy in the dilute limit  $\phi \rightarrow 0$ . In the third line of eq 2.7, we

give the entropic free energy of dissociation,<sup>5–7</sup> where  $v_0^{-1}\nu_M\phi$  is the density of the ionizable monomers.

**Solvation Interaction.** We have introduced the molecular interaction terms ( $\propto g_i$ ), which will be simply called the solvation interaction terms. In low-molecular-weight binary mixtures with salt,<sup>13,14</sup> such terms arise from the composition dependence of the solvation chemical potential of ions  $\mu_i^{\text{sol}}$ , where  $i$  represents the ion species. The original Born theory<sup>31</sup> gave  $\mu_i^{\text{sol}} = Z_i^2 e^2 / 2\epsilon(\phi) R_i$ , where  $Z_i e$  is the ion charge and  $R_i$  is called the Born radius. Here,  $R_i$  is on the order of 1 Å for small metallic ions in aqueous solution.<sup>8</sup> For each ion species, the difference of  $\mu_i^{\text{sol}}$  in the coexisting two phases is the Gibbs transfer free energy that is typically much larger than  $T$  per ion ( $\sim 15T$  for monovalent ions) in electrochemistry.<sup>32,33</sup> In polymer solutions, the origin of these terms can be more complex.<sup>21,22,34</sup> For example, ions interact with the dipoles of the solvent molecules and those on the chains differently, affecting the hydrogen bonding around the chains. Therefore, the solvation chemical potential of a charged particle of the species  $i$  ( $i = c, 1, 2, p$ ) arises from the interaction with the solvent molecules and that with the uncharged monomers as

$$\mu_i^{\text{sol}} = \epsilon_i^s(1 - \phi) + \epsilon_i^m\phi = (\epsilon_i^m - \epsilon_i^s)\phi + \epsilon_i^s \quad (2.12)$$

where  $\epsilon_i^m$  and  $\epsilon_i^s$  are the interaction energies. The solvation contribution to the free energy is given by the space integral of the sum

$$\sum_i \mu_i^{\text{sol}} n_i = T \sum_i g_i \phi n_i + \sum_i \epsilon_i^s n_i \quad (2.13)$$

Here, we find  $g_i$  appearing in eq 2.7 expressed as

$$g_i = (\epsilon_i^m - \epsilon_i^s) / T \quad (2.14)$$

The last term on the right-hand side of eq 2.12 contributes to a constant (irrelevant) chemical potential for  $i = 1, 2$  and to the constant  $\Delta_0$  in eq 2.7 for  $i = c, p$  (with the aid of eq 2.6 for  $i = c$ ). As a result, we have attraction for  $g_i < 0$  and repulsion for  $g_i > 0$  between the ions ( $i = c, 1, 2$ ) and the polymer chains, while we have a composition-dependent dissociation constant from  $i = c, p$  (see eq 2.27). For water-like solvent,  $g_i > 0$  for hydrophilic ions and  $g_i < 0$  for hydrophobic ions. The Born theory<sup>31</sup> and the data of the Gibbs transfer free energy<sup>32,33</sup> both suggest that  $|g_i|$  mostly much exceeds unity and is even larger for multivalent ions such as  $\text{Ca}^{2+}$ .

**B. Equilibrium Relations.** As a typical experimental geometry, our fluid system is inserted between two parallel metal plates with area  $S$  and separation distance  $L$  (much shorter than the lateral dimension  $S^{1/2}$ ). If the surface charge densities at the upper and lower plates are fixed at  $\pm\sigma_0$ , the electrostatic energy  $F_e = \int d\mathbf{r} \epsilon(\phi) \mathbf{E}^2 / 8\pi$  is a function of  $\phi$  and  $\rho$ . The potential values at the two plates are laterally homogeneous but are fluctuating quantities.<sup>14</sup>

For small variations  $\delta\phi$  and  $\delta\rho$  superimposed on  $\phi$  and  $\rho$ , the incremental change of  $F_e$  is written as<sup>14</sup>

$$\delta F_e = \int d\mathbf{r} \left[ \Phi \delta\rho - \frac{\epsilon_1 \mathbf{E}^2}{8\pi} \delta\phi \right] \quad (2.15)$$

Under the charge neutrality  $\int d\mathbf{r} \rho = 0$ , we first minimize  $F$  with respect to  $\zeta$  (or  $n_p$ ) and  $n_c$  at fixed  $n_1, n_2$ , and  $\phi$ . It is convenient to introduce  $G = F + (T\lambda/e) \int d\mathbf{r} \rho$ , where  $T\lambda/e$  is the Lagrange multiplier independent of space. Using eq 2.15, we may calculate  $\delta G / \delta\zeta$  and  $\delta G / \delta n_c$ . Setting them equal to 0, we obtain

$$\frac{\zeta}{1 - \zeta} = \exp[U + \lambda - \Delta_0 - g_p \phi] \quad (2.16)$$

$$n_c = v_0^{-1} \exp[-U - \lambda - g_c \phi] \quad (2.17)$$

where we introduce the normalized electric potential by

$$U = e\Phi / T \quad (2.18)$$

Next, homogeneity of the ion chemical potentials  $\mu_i = \delta F / \delta n_i$  ( $i = 1, 2$ ) yields

$$n_i = n_i^0 \exp[-g_i \phi - Z_i(U + \lambda)] \quad (2.19)$$

where  $n_i^0 = v_0^{-1} e^{u_i/T}$  are constants. Here,  $U$  and  $\lambda$  appear in the combination  $U + \lambda$  in all of the physical quantities. If  $U + \lambda$  is redefined as  $U$ ,  $\lambda$  may be set equal to 0 without loss of generality.

We also require homogeneity of  $h = \delta F / \delta\phi$ , where we fix  $n_c, n_1, n_2$ , and  $n_p$  in the functional derivative. With the aid of eq 2.15, some calculations give

$$\frac{h}{T} = \frac{1}{T} f'_0(\phi) + \frac{C'}{2} |\nabla\phi|^2 - \nabla \cdot C \nabla\phi - \frac{\epsilon_1}{8\pi T} E^2 + \sum_{i=c,1,2,p} g_i n_i + v_0^{-1} \nu_M \ln(1 - \zeta) \quad (2.20)$$

where  $f'_0 = \partial f_0 / \partial\phi$  and  $C' = \partial C / \partial\phi$ . On the right-hand side, the first three terms are those in the usual Ginzburg–Landau theory.<sup>26</sup> The last three terms arise from the electrostatic interaction, the solvation interaction, and the dissociation equilibration, respectively. We may calculate the interface profiles and the mesophase profiles from the homogeneity of  $h$ .<sup>14</sup>

**Surface Tension.** In the above procedure, we have minimized the grand potential  $\Omega = \int d\mathbf{r} \omega$  under the charge neutrality  $\int d\mathbf{r} \rho = 0$ , where the grand potential density is defined by

$$\omega = f_T - h\phi - \mu_1 n_1 - \mu_2 n_2 \quad (2.21)$$

with  $f_T$  being given by eq 2.7. Using eqs 2.16–2.19, we may eliminate  $\mu_1$  and  $\mu_2$  to obtain

$$\omega = f_0 + \frac{TC}{2} |\nabla\phi|^2 - h\phi + \frac{\epsilon_1}{8\pi} E^2 - \rho\Phi - T \sum_{i=c,1,2} n_i + T v_0^{-1} \nu_M \phi \ln(1 - \zeta) \quad (2.22)$$

Furthermore, using eq 2.20, we may calculate the space gradient of  $\omega$  as

$$\frac{\partial \omega}{\partial x_k} = \sum_l \frac{\partial}{\partial x_l} \left( TC \frac{\partial \phi}{\partial x_k} \frac{\partial \phi}{\partial x_l} \right) - \frac{\partial}{\partial x_k} \rho U \quad (2.23)$$

where  $\partial/\partial x_k$  and  $\partial/\partial x_l$  are the space derivatives with respect to the Cartesian coordinates  $x$ ,  $y$ , and  $z$ . In the one-dimensional case, where all of the quantities vary along the  $z$  axis, the above equation is integrated to give

$$\omega = TC(\phi')^2 - \rho\Phi + \omega_\infty \quad (2.24)$$

where  $\phi' = d\phi/dz$  and  $\omega_\infty$  is a constant. Therefore, around a planar interface separating two bulk phases,  $\omega(z)$  tends to a common constant  $\omega_\infty$  as  $z \rightarrow \pm\infty$ . From the above relation, the surface tension  $\gamma = \int dz[\omega(z) - \omega_\infty]$  is expressed as

$$\begin{aligned} \frac{\gamma}{T} &= 2 \int dz \left[ \frac{\hat{f}_0}{T} - \sum_{i=c,1,2} n_i + \frac{\nu_M \phi}{\nu_0} \ln(1 - \zeta) \right] \\ &= \int dz [C(\phi')^2 - \frac{\varepsilon(\phi)}{4\pi T} E^2] \end{aligned} \quad (2.25)$$

where  $\hat{f}_0 = f_0 - h\phi - \omega_\infty$  in the first line and use is made of  $\int dz \rho\Phi = \int dz \varepsilon E^2/4\pi$ . In the second line, the integrand consists of a positive gradient term and a negative electrostatic term. Similar expressions for the surface tension have been obtained for electrolytes<sup>14</sup> and ionic surfactant systems.<sup>15</sup>

**Mass Action Law.** If eqs 2.16 and 2.17 are multiplied,  $U$  cancels to disappear. It follows the equation of ionization equilibrium or the mass action equation<sup>6,7</sup>

$$\frac{\zeta}{1 - \zeta} n_c = K(\phi) \quad (2.26)$$

where  $K(\phi)$  is the dissociation constant of the form

$$K(\phi) = \nu_0^{-1} \exp[-\Delta_0 - (g_p + g_c)\phi] \quad (2.27)$$

We may interpret  $\Delta(\phi) \equiv \Delta_0 + (g_p + g_c)\phi$  as the composition-dependent dissociation energy divided by  $T$ . With increasing  $\phi$ , the dissociation decreases for positive  $g_p + g_c$  and increases for negative  $g_p + g_c$ . If  $g_p + g_c \gg 1$ ,  $K(\phi)$  decreases greatly even for a small increase of  $\phi$ . Then  $\zeta$  and  $n_p$  are related to  $n_c$  as

$$\zeta = \frac{\nu_0 n_p}{\nu_M \phi} = \frac{K}{K + n_c} \quad (2.28)$$

These relations hold in equilibrium states, which may be inhomogeneous. In our theory,  $n_p = n_p(\phi, U)$  is a function of the local values of  $\phi$  and  $U$  as well as  $n_c$ ,  $n_1$ , and  $n_2$ . Here

$$\frac{\partial n_p}{\partial U} = (1 - \zeta)n_p \quad \frac{\partial n_p}{\partial \phi} = \frac{n_p}{\phi} - (1 - \zeta)g_p n_p \quad (2.29)$$

Therefore,  $n_p$  increases with increasing  $U$  at fixed  $\phi$ .

**Relations in Bulk without Salt.** Furthermore, in a homogeneous bulk phase with  $n_p = n_c$ , eq 2.28 yields the quadratic equation for  $n_c$

$$n_c(n_c + K) = \nu_0^{-1} \nu_M \phi K \quad (2.30)$$

which is solved to give

$$\zeta = \frac{\nu_0 n_c}{\nu_M \phi} = \frac{2}{\sqrt{Q + 1} + 1} \quad (2.31)$$

Here, it is convenient to introduce

$$Q(\phi) = 4\nu_M \phi / \nu_0 K(\phi) \quad (2.32)$$

In particular, we find  $\zeta \ll 1$  and  $n_c \cong (\nu_M \phi K / \nu_0)^{1/2}$  for  $Q \gg 1$ , while  $\zeta \rightarrow 1$  for  $Q \ll 1$ . Thus, the ion density  $n_c$  has been determined for a given  $\phi$ .

**Relations in Bulk with Salt.** As another simple situation, we may add a salt whose cations are of the same species as the counterions. The cations and anions are both monovalent. Here, the counterions and the cations from the salt are indistinguishable. Thus, the sum of the counterion density  $n_c$  and the salt cation density  $n_1$  is written as  $n_c$ , while the salt anion density is written as  $n_2$ . The charge neutrality condition becomes  $n_c = n_p + n_2$  in the bulk. From eq 2.28, we obtain

$$n_c = \nu_0^{-1} \nu_M \phi K / (K + n_c) + n_2 \quad (2.33)$$

in the bulk phase. Then,  $n_c$  increases with increasing  $n_2$ . We treat  $n_2$  as an externally given constant to obtain

$$\begin{aligned} n_c &= \frac{1}{2}(n_2 - K) + \frac{1}{2}\sqrt{(n_2 + K)^2 + 4\nu_0^{-1} \nu_M \phi K} \\ &\cong n_2 + \nu_0^{-1} \nu_M \phi K / (n_2 + K) \end{aligned} \quad (2.34)$$

where the second line holds in the case of  $n_2 + K \gg 2(\nu_M \phi K / \nu_0)^{1/2} = Q^{1/2}K$ . With increasing  $n_2$ , the ionized monomer density  $n_p = n_c - n_2$  decreases, while  $n_c$  increases. At high salt densities, where  $n_2$  greatly exceeds both  $2(\nu_M \phi K / \nu_0)^{1/2}$  and  $K$ , we eventually obtain

$$n_c \cong n_2 \quad n_p \cong \nu_M \frac{K\phi}{n_2} \ll n_2 \quad \zeta \cong \frac{K}{n_2} \ll 1 \quad (2.35)$$

### III. Structure Factor of Composition Fluctuations

In phase-transition theories,<sup>26</sup> the order parameter fluctuations obey the equilibrium distribution  $\propto \exp(-F/T)$ , where  $F$  is the Ginzburg–Landau free energy functional. In the present problem, the thermal fluctuations of  $\phi$ ,  $n_i$ , and  $\zeta$  are assumed to obey the distribution  $\propto \exp(-F/T)$  in equilibrium, where  $F$  is the space integral of  $f_T$  in eq 2.7. In the Gaussian approximation of  $F$ , we consider small plane wave fluctuations of  $\phi$ ,  $n_i$ , and  $\zeta$  with wave vector  $\mathbf{q}$  in a one-phase state. It then follows the mean-field expression for the structure factor  $S(q)$  of the composition fluctuations. It is of the form of eq 1.1 for a constant degree of ionization  $\zeta$  in the absence of the solvation interaction. Here, it will be calculated including the solvation interaction and in the annealed case. We examine how it depends on the parameters  $g_c$ ,  $g_1$ ,  $g_2$ , and  $g_p$  and how it is modified by the fluctuating ionization.

**A. Gaussian Approximation.** From eq 2.7, the fluctuation contributions to  $F$  in the bilinear order are written as

$$\frac{\delta F}{T} = \sum_q \left[ \frac{1}{2}(\bar{r} + Cq^2)|\phi_q|^2 + \frac{2\pi}{\epsilon q^2}|\rho_q|^2 + \sum_{i=c,1,2} \frac{|n_{iq}|^2}{2n_i} + \sum_{i=c,1,2,p} g_i n_{iq} \phi_q^* + \frac{n_p}{2(1-\zeta)\zeta^2} |\zeta_q|^2 \right] \quad (3.1)$$

where  $\phi_q$ ,  $\rho_q$ ,  $n_{iq}$  ( $i = c, 1, 2, p$ ), and  $\zeta_q$  are the Fourier components of  $\phi(\mathbf{r})$ ,  $\rho(\mathbf{r})$ ,  $n_i(\mathbf{r})$ , and  $\zeta(\mathbf{r})$ , respectively. From eq 2.4, the fluctuation of the charged monomer density is of the form

$$n_{pq} = \frac{n_p}{\zeta} \zeta_q + \frac{n_p}{\phi} \phi_q \quad (3.2)$$

In this section,  $\phi$  and  $n_i$  denote the spatial averages, where  $n_p = \sum_{i=c,1,2} Z_i n_i$  from the overall charge neutrality. The inhomogeneity in the dielectric constant may be neglected for small fluctuations. From the Flory–Huggins free energy (eq 2.8), the coefficient  $\bar{r}$  is of the form

$$\nu_0 \bar{r} = \frac{\nu_0 \partial^2 f_0}{T \partial \phi^2} = \frac{1}{N\phi} + \frac{1}{1-\phi} - 2\chi \quad (3.3)$$

On the right-hand side of eq 3.1, the first term yields the Ornstein–Zernike structure factor of the composition without the coupling to the charged particles. The second and third terms are well-known for electrolyte systems, leading to the Debye–Hückel screening of the charge density correlation. The fourth term arises from the solvation interaction, while the fifth term is from the fluctuation of ionization.

We minimize  $\delta F$  with respect to  $n_{iq}$  ( $i = c, 1, 2, p$ ) at fixed  $\phi_q$  to express them in the linear form  $n_{iq} \propto \phi_q$ . In particular,  $\rho_q$  and  $\zeta_q$  are written as

$$\rho_q = \frac{q^2}{4\pi l_B} U_q = -\frac{Aq^2}{q^2 + \kappa_T^2} \phi_q \quad (3.4)$$

$$\zeta_q = -\zeta(1-\zeta) \left[ g_p + \frac{4\pi l_B A}{q^2 + \kappa_T^2} \right] \phi_q \quad (3.5)$$

where  $U_q$  is the Fourier component of  $U(\mathbf{r})$  and

$$\kappa_T^2 = 4\pi l_B [(1-\zeta)n_p + \sum_{i=c,1,2} Z_i n_i] \quad (3.6)$$

$$A = \frac{n_p}{\phi} - (1-\zeta)g_p n_p + \sum_{i=c,1,2} Z_i g_i n_i \quad (3.7)$$

Here,  $\kappa_T$  defined in eq 3.6 is a generalized Debye–Hückel wavenumber introduced by Raphael and Joanny,<sup>5</sup> where the term proportional to  $n_p$  arises from dissociation and recombination on the polymer chains. The first relation (eq 3.4) itself readily follows from the relations

$$\frac{\partial \rho}{\partial \phi} = -eA \quad \frac{\partial \rho}{\partial U} = -\frac{e\kappa_T^2}{4\pi l_B} \quad (3.8)$$

where  $\rho(\mathbf{r})$  is regarded as a function of the local values of  $U(\mathbf{r})$  and  $\phi(\mathbf{r})$  as discussed around eqs 2.28 and 2.29. From eq 3.5, we find  $\zeta_q \rightarrow 0$  as  $\zeta \rightarrow 0$  or 1. We can see that the last term on the right-hand side of eq 3.1 is negligible as  $\zeta \rightarrow 1$ .

After elimination of  $n_{iq}$  ( $i = c, 1, 2, p$ ), the free energy change  $\delta F$  is expressed as  $\delta F = \sum_q T|\phi_q|^2/S(q)$ , where  $S(q)$  is the composition structure factor calculated as

$$\begin{aligned} \frac{1}{S(q)} &= \bar{r} + r_s + Cq^2 + \frac{4\pi l_B A^2}{q^2 + \kappa_T^2} \\ &= \bar{r} + r_s + C\gamma_p^2 \kappa_T^2 + Cq^2 \left[ 1 - \frac{\gamma_p^2 \kappa_T^2}{q^2 + \kappa_T^2} \right] \end{aligned} \quad (3.9)$$

where  $r_s$  is the shift of  $\bar{r}$  arising from the solvation interaction given by

$$r_s = [2\phi^{-1}g_p - (1-\zeta)g_p^2]n_p - \sum_{i=c,1,2} g_i^2 n_i \quad (3.10)$$

As  $\phi \rightarrow 0$ , we have  $r_s \cong 2g_p f$ . For large  $|g_i| \gg 1$ , the other negative terms ( $\propto g_i^2$ ) can be significant, leading to  $r_s < 0$ . In the second line of eq 3.9,  $\gamma_p$  is defined by

$$\gamma_p = \sqrt{\frac{4\pi l_B A}{C \kappa_T^2}} = \frac{(4\pi l_B C)^{-1/2} A}{(1-\zeta)n_p + \sum_{i=c,1,2} Z_i n_i} \quad (3.11)$$

where  $(4\pi l_B C)^{-1/2} = [3a\phi(1-\phi)/\pi l_B]^{1/2}$  if use is made of eq 2.9. Note that  $r_s$  and  $\kappa_T^2$  consist of the terms proportional to the charge densities, while  $\gamma_p$  depends on their ratios. In particular, if  $n_c = n_p$  and  $n_1 = n_2$  in the monovalent case,  $\gamma_p$  depends on the density ratio  $R \equiv n_1/n_p$  as

$$\gamma_p = \frac{(4\pi l_B C)^{-1/2}}{2-\zeta+2R} \left[ \frac{1}{\phi} - (1-\zeta)g_p + g_c + (g_1 - g_2)R \right] \quad (3.12)$$

Here,  $R = 0$  for salt-free polyelectrolytes, and  $R$  increases with increasing salt density. As  $R \rightarrow \infty$ , the above formula tends to that for neutral polymer solutions (low-molecular-weight binary mixtures for  $N = 1$ ) with salt. We note that  $\gamma_p$  can even be negative depending on the solvation terms in the brackets on the right-hand side of eq 3.12.

**B. Macrophase and Microphase Separation.** From the second line of eq 3.9, we obtain the small- $q$  expansion  $S(q)^{-1} = a_0 + a_1 q^2 + a_2 q^4 \dots$  with

$$a_1 = C(1 - \gamma_p^2) \quad (3.13)$$

Therefore, we encounter the following two cases. (i) If  $|\gamma_p| < 1$ ,  $S(q)$  is maximum at  $q = 0$ , and we predict the usual phase transition with increasing  $\chi$  in the mean-field theory. The spinodal  $\chi = \chi_{sp}$  is given by

$$2\chi_{\text{sp}} = \frac{1}{N\phi} + \frac{1}{1-\phi} + r_s + C\gamma_p^2\kappa_T^2 \quad (3.14)$$

Macroscopic phase separation occurs for  $\chi > \chi_{\text{sp}}$ . On the right-hand side of eq 3.14,  $r_s = 0$ , and the last term becomes  $n_p/(1-\zeta)\phi^2 > 0$  for  $g_i = 0$ , but the sum of the last two terms can be much altered for  $|g_i|\phi \gtrsim 1$ . For example, without salt and in the monovalent case, it is equal to  $[1/\phi^2 + \zeta g_c^2 + 2g_s/\phi]n_p/(1-\zeta) - 2g_p g_c n_p$ . (ii) If  $|\gamma_p| > 1$ ,  $S(q)$  has a peak at an intermediate wavenumber  $q_m$  given by

$$q_m^2 = (4\pi l_B C)^{1/2} |A| - \kappa_T^2 = \kappa_T^2 (|\gamma_p| - 1) \quad (3.15)$$

Thus,  $q_m \rightarrow 0$  as  $\kappa_T \rightarrow 0$  or as  $|\gamma_p| \rightarrow 1$ . The spinodal is given by  $S(q_m)^{-1} = 0$  or by

$$2\chi_{\text{sp}} = \frac{1}{N\phi} + \frac{1}{1-\phi} + r_s + C\kappa_T^2 (2|\gamma_p| - 1) \quad (3.16)$$

Microphase separation should be triggered for  $\chi > \chi_{\text{sp}}$ . Since  $\gamma_p$  depends only on the ion density ratio  $R$  as in eq 3.12, the criterion  $\gamma_p > 1$  remains unchanged no matter how small the densities of the charged particles. Of course, mesophase formation is well-defined only when  $q_m$  in eq 3.15 is much larger than the inverse of the system length. In the following, we discuss some special cases.

**Polyelectrolytes without Solvation Interaction.** For  $g_i = 0$ , we have  $r_s = 0$  and  $A = n_p/\phi = v_0^{-1}f$  as in the previous theories of weakly ionized polyelectrolytes.<sup>5,9,10</sup> In the monovalent case, eq 3.12 gives

$$\begin{aligned} \gamma_p &= 1/[4\pi l_B C]^{1/2} (2 - \zeta + 2R)\phi \\ &= [3a\phi/\pi l_B (1 - \phi)]^{1/2} / (2 - \zeta + 2R) \end{aligned} \quad (3.17)$$

where  $R = n_i/n_p$  and use is made of eq 2.9 in the second line. Here,  $\gamma_p$  is largest without salt ( $R = 0$ ) and decreases with increasing  $R$ . In accord with this predicted salt effect, Braun et al.<sup>19</sup> observed a mesophase at low salt concentration and a macroscopic phase separation at high salt concentration. However, for large  $|g_i|$ , the solvation interaction comes into play. Thus, more experiments are desirable to detect it in polyelectrolytes with water-like solvent.

**Binary Mixtures with Solvation Interaction.** Without ionization or for  $f = 0$ , we have  $n_p = n_c = 0$ . Here, we describe a neutral binary mixture with salt. Further, for a monovalent salt, we have  $A = (g_1 - g_2)n_1$  and

$$\gamma_p = (g_1 - g_2)/(16\pi l_B C)^{1/2} \quad (3.18)$$

$$r_s = -(g_1^2 + g_2^2)n_1 \quad (3.19)$$

From neutron scattering, Sadakane et al.<sup>20</sup> found periodic structures in a near-critical, low-molecular-weight mixture of D<sub>2</sub>O and trimethylpyridine (3MP) containing sodium tetrarphenylborate (NaBPh<sub>4</sub>). Their salt is composed of the strongly hydrophilic cation Na<sup>+</sup> and the strongly hydrophobic anion BPh<sub>4</sub><sup>-</sup>. If their data are interpreted in our theoretical scheme, we expect  $g_1 \gg 1$ ,  $g_2 \ll -1$ , and  $\gamma_p > 1$  for their system. Such

ion pairs are antagonistic to each other, undergoing microphase separation where the solvent composition is inhomogeneous. It is worth noting that the scattering amplitude was maximum at  $q = 0$  upon addition of NaCl, KCl, and so forth in the same mixture of D<sub>2</sub>O–3MP.<sup>35</sup> These salts consist of hydrophilic anions and cations with  $g_1 \sim g_2$ ; therefore,  $\gamma_p$  should be much smaller, leading to no mesophase formation. It is also striking that the coexistence curve is greatly shifted as  $\Delta T \propto r_s \propto g_i^2$  for large  $|g_i|$  with increasing the salt density even for hydrophilic ion pairs, which is consistent with a number of previous experiments.<sup>36–38</sup>

**Neutral Polymer Solutions with Salt.** For very weak ionization but in the presence of salt,  $\gamma_p$  is expressed as in eq 3.18. In our theory, even polymer solutions consisting of neutral polymers and a polar solvent can exhibit a charge density wave phase for  $|g_1 - g_2| \gg 1$ . Hakim et al.<sup>21,22</sup> found a broad peak at an intermediate wavenumber in the scattering amplitude in (neutral) polyethylene oxide (PEO) solutions with methanol and with acetonitrile by adding a small amount of salt KI. They ascribed the origin of the peak to the binding of potassium ions to PEO chains. In our theory, such a peak can arise for a sufficiently large  $g_1 - g_2$ . Remarkably, the peak disappeared if the solvent was water, which indicates a sensitive dependence of the molecular interactions on the solvent species. Thus, more experiments should be informative, where use of antagonistic ion pairs will yield more drastic effects, leading to mesophases.

#### IV. One-Dimensional Profiles and Numerical Results

We give numerical results of one-dimensional profiles in equilibrium. All of the quantities are assumed to vary along the  $z$  axis. For each given  $\phi(z)$ , we need to solve the nonlinear Poisson equation (eq 2.10) numerically. The charge density is expressed as

$$\rho(z) = e \sum_{i=c,1,2} Z_i n_i(z) - \frac{e\nu_M \phi(z)}{1 + n_c(z)/K(z)} \quad (4.1)$$

where  $n_i(z) \propto \exp[-g_i \phi(z) - Z_i U(z)]$  from eqs 2.17 and 2.19 and  $K(z)$  depends on  $\phi(z)$  as in eq 2.27. We then seek  $\phi(z)$  self-consistently from the homogeneity of the right-hand side of eq 2.20.

As in electrolytes, there appears to be a difference of the electric potential  $\Delta\Phi$  across an interface, which is called the Galvani potential difference.<sup>14</sup> Because there are many parameters, we will set  $\chi = 1$ ,  $N = 20$ ,  $\epsilon_1 = -0.9\epsilon_0$ , and  $l_B = e^2/\epsilon_0 T = 8a/\pi$  in all of the following examples. Then, the dielectric constant of the solvent is 10 times larger than that of the polymer. The space will be measured in units of the molecular size  $a = v_0^{1/3}$ .

**A. Interface without Salt.** First, we suppose coexistence of two salt-free phases, separated by a planar interface. Hereafter, the quantities with the subscript  $\alpha$  (the subscript  $\beta$ ) denote the bulk values in the polymer-rich (solvent-rich) phase attained as  $z \rightarrow -\infty$  (as  $z \rightarrow \infty$ ). Namely, we write  $n_{c\alpha} = n_c(-\infty)$  and  $n_{c\beta} = n_c(\infty)$ . Here, we obtain  $n_{c\alpha}$  or  $n_{c\beta}$  from eq 2.29 and

$$\frac{n_{c\alpha}}{n_{c\beta}} = \frac{\phi_\alpha \tilde{\zeta}_\alpha}{\phi_\beta \tilde{\zeta}_\beta} = \exp(-g_c \Delta\phi - \Delta U) \quad (4.2)$$

from eq 2.17. Hereafter,  $\Delta\phi = \phi_\alpha - \phi_\beta$  is the composition difference and

$$\Delta U = e\Delta\Phi/T = e(\Phi_\alpha - \Phi_\beta)/T \quad (4.3)$$

is the normalized Galvani potential difference. In terms of  $Q_\alpha = 4\nu_M\phi_\alpha/v_0K_\alpha$  and  $Q_\beta = 4\nu_M\phi_\beta/v_0K_\beta$ , we obtain

$$\Delta U = g_p\Delta\phi + \ln\left[\frac{\sqrt{Q_\beta + 1} - 1}{\sqrt{Q_\alpha + 1} - 1}\right] \quad (4.4)$$

$$\frac{n_{c\beta}}{n_{c\alpha}} = \frac{\phi_\beta(\sqrt{Q_\alpha + 1} + 1)}{\phi_\alpha(\sqrt{Q_\beta + 1} + 1)} \quad (4.5)$$

In particular, if  $Q_\alpha \gg 1$  and  $Q_\beta \gg 1$  (or  $\zeta_\alpha \ll 1$  and  $\zeta_\beta \ll 1$ ), we obtain  $\Delta U \cong (g_p - g_c)\Delta\phi/2 + \ln(\phi_\beta/\phi_\alpha)$  and  $n_{c\beta}/n_{c\alpha} \cong \exp[(g_p + g_c)\Delta\phi/2](\phi_\beta/\phi_\alpha)^{1/2}$ .

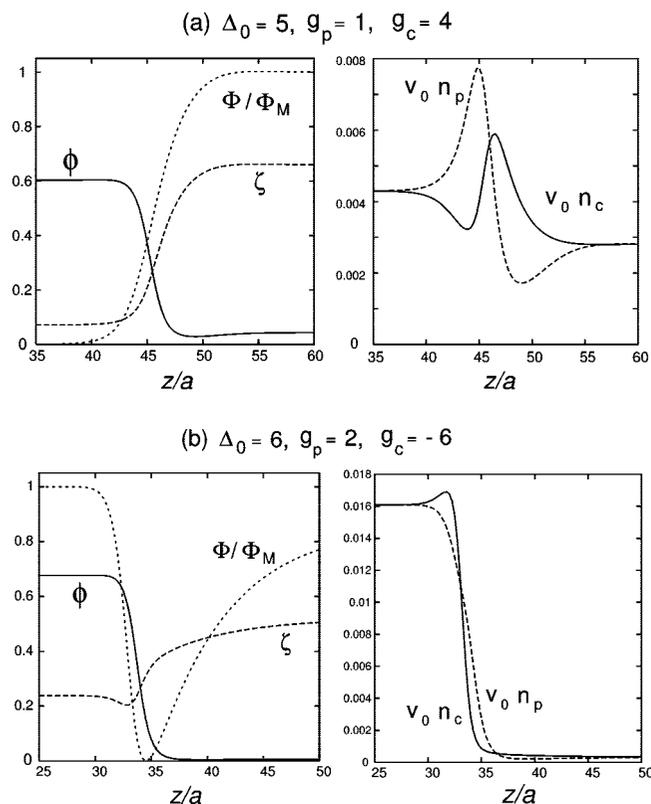
The interface profiles are extremely varied, sensitively depending on the molecular interaction parameters,  $\Delta_0$ ,  $g_p$ , and  $g_c$ . As such examples, in Figure 1, we show salt-free interface profiles for (a)  $\Delta_0 = 5$ ,  $g_p = 1$ , and  $g_c = 4$  and (b)  $\Delta_0 = 8$ ,  $g_p = 2$ , and  $g_c = -6$ . In the  $\alpha$  and  $\beta$  regions, the degree of ionization  $\zeta$  is 0.071 and 0.65 in (a) and is 0.24 and 0.51 in (b), respectively. The charge densities are multiplied by  $v_0 = a^3$ . The  $\Delta U = e(\Phi_\alpha - \Phi_\beta)/T$  is  $-2.67$  in (a) and  $0.099$  in (b). Interestingly, in (b),  $U(z)$  exhibits a deep minimum with  $U_{\min} = U_\beta - 5.98$  at the interface position. We can see the appearance of the charge density  $n_c - n_p$  around the interface, resulting in an electric double layer. The counterion density is shifted to the  $\beta$  region in (a) because of positive  $g_c$  and to the  $\alpha$  region in (b) because of negative  $g_c$ . The parameter  $\gamma_p$  in eq 3.11 is 0.75 in (a) and 0.20 in (b) in the  $\alpha$  region, ensuring the stability of the  $\alpha$  region. From eq 2.25, the surface tension  $\gamma$  is calculated as  $\gamma = 0.0175T/a^2$  in (a) and as  $0.0556T/a^2$  in (b), while we obtain  $\gamma = 0.050T/a^2$  without ions at the same  $\chi = 1$ . In (a), the surface tension  $\gamma$  is largely decreased because the electrostatic term in eq 2.25 is increased due to the formation of a large electric double layer. In (b), on the contrary, it is increased by 10% due to depletion of the charged particles from the interface.<sup>14</sup>

**B. Interface with Salt.** With addition of salt, interface profiles are even more complex. For simplicity, we consider a salt whose cations are of the same species as the counterions from the polymer. This is the example discussed at the end of section II. The free energy density in this case is still given by eq 2.7 if we set  $n_1 = 0$  there. The densities of the mobile cations, the mobile anions, and the charged monomers are written as  $n_c(z)$ ,  $n_2(z)$ , and  $n_p(z)$ , respectively. All of the charged particles are monovalent. We treat  $n_{2\beta}$  in the solvent-rich  $\beta$  region as a control parameter, which is the salt density added in the  $\beta$  region. The densities  $n_2(z)$  and  $n_c(z)$  depend on  $z$  as

$$\begin{aligned} n_2(z) &= n_{2\beta} \exp[g_2(\phi_\beta - \phi(z)) - U_\beta + U(z)] \\ n_c(z) &= n_{c\beta} \exp[g_c(\phi_\beta - \phi(z)) + U_\beta - U(z)] \end{aligned} \quad (4.6)$$

We write  $S \equiv n_{2\beta}/K_\beta$  to avoid the cumbersome notation in the following. Use of the first line of eq 2.34 gives

$$n_{c\beta} = \frac{K_\beta}{2} \left[ S - 1 + \sqrt{(S + 1)^2 + Q_\beta} \right] \quad (4.7)$$



**Figure 1.** Interface profiles in the salt-free case for (a)  $\Delta_0 = 5$ ,  $g_p = 1$ , and  $g_c = 4$  (top) and for (b)  $\Delta_0 = 8$ ,  $g_p = 2$ , and  $g_c = -6$  (bottom). Polymer volume fraction  $\phi(z)$ , normalized potential  $\Phi(z)/\Phi_M$ , and degree of ionization  $\zeta(z)$  (left) and normalized charge densities  $v_0 n_c(z)$  and  $v_0 n_p(z)$  (right). The other parameters are common as  $\chi = 1$ ,  $N = 20$ ,  $\nu_M = 0.1$ ,  $\epsilon_1 = -0.9\epsilon_0$ , and  $l_B = 8a/\pi$ . Here,  $\Phi(z)$  is measured from its minimum, and  $\Phi_M (= 2.67T/e$  in (a) and  $6.86T/e$  in (b)) is the difference of its maximum and minimum.

We use eq 2.33 in the  $\alpha$  region to determine  $n_{c\alpha}$ . Since  $n_{c\alpha}n_{2\alpha}/K_\alpha = n_{c\beta}n_{2\beta}/K_\beta$  from eq 4.5,  $n_{c\alpha}$  obeys

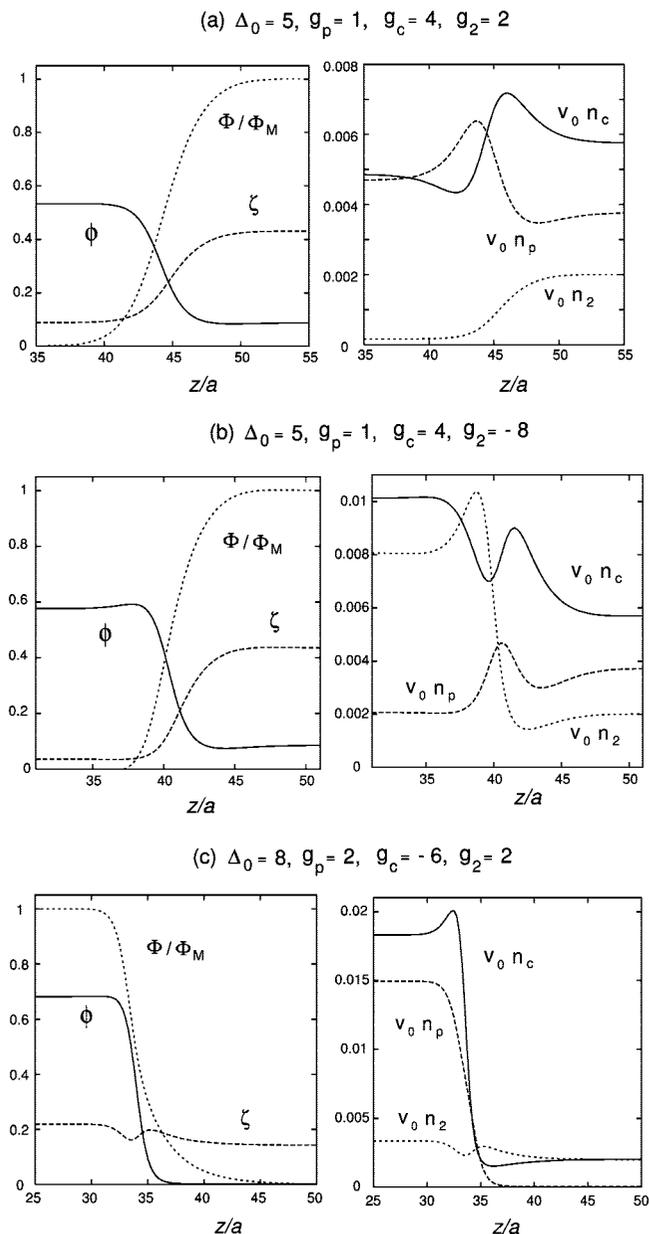
$$(n_{c\alpha} - S n_{c\beta} K_\alpha / n_{c\alpha})(1 + n_{c\alpha}/K_\alpha) = v_0^{-1} \nu_M \phi_\alpha \quad (4.8)$$

In particular, if  $n_{c\alpha} \gg K_\alpha$  or if  $\zeta_\alpha \ll 1$ , we find

$$n_{c\alpha} \cong K_\alpha^{1/2} (S n_{c\beta} + v_0^{-1} \nu_M \phi_\alpha)^{1/2} \quad (4.9)$$

$$\Delta U \cong g_p \Delta\phi + \frac{1}{2} \ln \left[ \frac{n_{c\beta}^2 / K_\beta^2}{S n_{c\beta} / K_\alpha + Q_\alpha} \right] \quad (4.10)$$

In Figure 2, we show profiles of  $\phi(z)$ ,  $\Phi(z)$ ,  $\zeta(z)$ ,  $n_c(z)$ ,  $n_2(z)$ , and  $n_p(z)$  with  $n_{2\beta} = 0.002v_0^{-1}$  held fixed for three cases, (a)  $\Delta_0 = 5$ ,  $g_p = 1$ ,  $g_c = 4$ , and  $g_2 = 2$ ; (b)  $\Delta_0 = 5$ ,  $g_p = 1$ ,  $g_c = 4$ , and  $g_2 = -8$ ; and (c)  $\Delta_0 = 8$ ,  $g_p = 2$ ,  $g_c = -6$ , and  $g_2 = 2$ . The normalized potential difference  $\Delta U$  is  $-1.61$  in (a),  $-2.54$  in (b), and  $1.88$  in (c), while the normalized surface tension  $a^2\gamma/T$  is given by  $0.0358$  in (a),  $0.0233$  in (b), and  $0.0554$  in (c). In (a), the cations and anions are both repelled from the interface into the  $\beta$  region because of positive  $g_c$  and  $g_2$ . In (b), owing to  $g_2 = -8$ , the anions become richer in the  $\alpha$  region than in the  $\beta$  region since they are strongly attracted to the polymer chains. There, despite  $g_c = 4$ , the cations become also richer in the  $\alpha$  region to satisfy the charge neutrality. In (c), we set  $g_c = -6$ ; therefore, the cations are strongly attracted to the



**Figure 2.** Interface profiles with mobile cations and anions for (a)  $\Delta_0 = 5$ ,  $g_p = 1$ ,  $g_c = 4$ , and  $g_2 = 2$  (top), for (b)  $\Delta_0 = 5$ ,  $g_p = 1$ ,  $g_c = 4$ , and  $g_2 = -8$  (middle), and for (c)  $\Delta_0 = 8$ ,  $g_p = 2$ ,  $g_c = -6$ , and  $g_2 = 2$  (bottom). Curves represent  $\phi(z)$ ,  $\Phi(z)/\Phi_M$  and  $\zeta(z)$  (left) and  $v_0 n_c(z)$ ,  $v_0 n_p(z)$ , and  $v_0 n_2(z)$  (right) with  $v_0 n_{2\beta} = 0.002$ . Here,  $\Phi(z)$  is measured from its minimum, and  $\Phi_M$  is the difference of its maximum and minimum. The other parameters are the same as those in Figure 1.

polymer chains. The cations are also attracted into the  $\alpha$  region. The electric dipole due to the double layer is reversed, yielding  $\Delta U = U_\alpha - U_\beta > 0$ .

**C. Periodic State.** With varying of the temperature (or  $\chi$ ), the average composition  $\langle \phi \rangle$ , and the amount of salt, there can emerge a number of mesophases sensitively depending on the various molecular parameters ( $g_i$ ,  $\Delta_0$ , and  $\nu_M$ ). In Figure 3, we show an example of a one-dimensional periodic state without salt. Here,  $\nu_M$  is set equal to 0.5, and the charge densities are greatly increased. In this case, the degree of segregation and the charge heterogeneities are much milder than those in the cases in Figure 1. Since the charge density  $\rho(z)$  everywhere remains small, eq 2.31 locally holds approximately. Thus

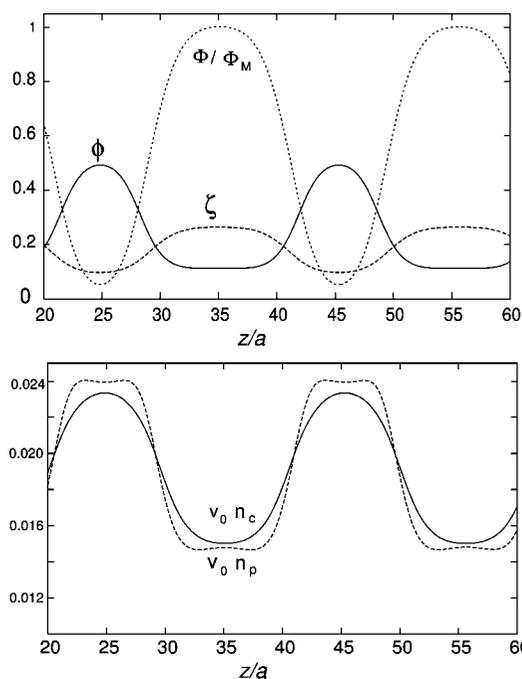
$$n_c(z) \cong \frac{\nu_M \phi(z)}{\sqrt{Q(z) + 1/4 + 1/2}} \quad (4.11)$$

where  $Q(z)$  is defined by eq 2.32 and  $n_p(z)$  is determined by eq 2.26. The deviation of  $n_c(z)$  from the right-hand side of eq 4.10 gives  $\Phi(z)$  as a first approximation. The above relation approximately holds slightly below the transition from a disordered state to a charge density wave state.

## V. Summary and Remarks

The charge distributions in polyelectrolytes are extremely complex around interfaces and in mesoscopic states, sensitively depending on the molecular (solvation) interaction and the dissociation process. Our continuum theory takes account of these effects in the simplest manner, though it should be inaccurate on the angstrom scale.

Our main results are as follows. In section II, we have presented a continuum theory accounting for the solvation effect and the dissociation equilibrium. The degree of ionization is rather a dynamic variable dependent on the local electric potential. The surface tension in eq 2.25 consists of a positive gradient term and a negative electrostatic term, where the latter is significant as the electric double layer is enhanced as in the top panels in Figures 1 and 2. In section III, we have calculated the structure factor  $S(q)$  of the composition fluctuations for polymer solutions with the solvation and ionization effects included. When the parameter  $\gamma_p$  in eq 3.11 or 3.12 exceeds unity in a one-phase state, a peak can appear at an intermediate wavenumber in  $S(q)$ . In such systems, a mesoscopic phase can emerge as the interaction parameter  $\chi$  is increased. In section IV, we have numerically solved the equilibrium equations in section II to examine one-dimensional profiles of interfaces with and without salt and in a periodic state without salt. Though very preliminary and fragmentary, our numerical results demonstrate the dramatic influence of the solvation interaction on inhomogeneous structures.



**Figure 3.** Periodic profiles in a salt-free mesophase with  $\nu_M = 0.5$ ,  $\Delta_0 = 5$ ,  $g_p = 1$ , and  $g_c = 4$ . Top:  $\phi(z)$ ,  $\Phi(z)/\Phi_M$  with  $\Phi_M = 0.867/e$  and  $\zeta(z)$ . Bottom:  $v_0 n_c(z)$  and  $v_0 n_p(z)$ .

A number of complex effects should be further taken into account to properly describe polyelectrolytes. (i) Under eq 2.1, we have neglected the effect of the electrostatic interaction on the chain conformations to use the Flory–Huggins free energy density. Hence, as argued in the literature,<sup>2,3</sup> our theory cannot be justified at small  $\phi$ . (ii) We have neglected the image interaction, which is known to increase the surface tension of a water–air interface at low ion densities.<sup>27</sup> Generally, it arises from a deformation of the self-interaction of ions due to inhomogeneous  $\epsilon$ .<sup>14</sup> Therefore, it originates from the discrete nature of ions and is not accounted for in the free energy eq 2.7, where the electric field  $\Phi$  is produced by the smoothly coarse-grained charge density  $\rho$ . (iii) At sufficiently low ion densities, we have neglected the ionic correlations giving rise to ion dipoles and clusters<sup>12,28</sup> and a free energy contribution due to the charge density fluctuations ( $\propto \kappa^3$ ).<sup>25,26</sup> (iv) The phase diagram of mesophases including the solvation interaction remains unknown. To describe the mesophases, we need to perform nonlinear analysis and computer simulations. (v) We have assumed a one-component water-like solvent. For two-component solvents, we may predict a variety of effects. For example, with the addition a small amount of water in a less polar solvent, hydration shells are formed around the hydrophilic ionized monomers and the counterions,<sup>8,33</sup> leading to an increase of the degree of ionization. For not small water concentrations, we may well predict formation of complex mesoscopic structures mediated by the Coulombic and solvation interactions.

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