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A Statistical Theory of Weakly Charged Polyelectrolytes: Fluctuations, Equation of State, and Microphase Separation

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ABSTRACT: A microscopic statistical theory of polyelectrolyte solutions (PES) with polyions of low linear charge density is developed in the random phase approximation (RPA). Correlation functions of a multicomponent PES and the fluctuational electrostatic contribution to the free energy of the system are calculated. Owing to the high-polymer nature of the system these expressions differ essentially from those of Debye–Huckel (DH) type. It is shown that under certain conditions a microphase separation into oppositely charged domains takes place in PES. The phase diagram is given. The expressions for the screened Coulomb potential of a test charge are obtained. In some cases the potential oscillates. The RPA is shown to be valid for intermediate monomer or salt concentrations and is violated at very low or very high concentrations.

I. Introduction

Great attention has been paid recently to the theoretical study of weakly charged polyelectrolyte solutions (PES).[1-6] The first theoretical consideration of a single weakly charged macromolecule in a solution was to our knowledge performed by de Gennes et al.[1] Then Pfeuty[2] took into account excluded-volume effects. The behavior of a single weakly charged macromolecule in a poor solvent, where counterion condensation of the avalanche type occurs, was studied by Khokhlov;[4] Khokhlov and Khachaturian[5] considered different fluctuation regimes of a weakly charged PES and constructed the diagram of states with variables: polymer concentration in the solution and concentration of the low molecular weight salt. In their paper the problem of the Debye–Huckel (DH) screening by nonlocal objects was also considered. However, in ref 5 the effects of the solvent quality on the properties of PES were discussed only briefly. In this paper we shall develop the statistical theory of the DH type for a sufficiently concentrated weakly charged PES. This will enable us not only to consider the properties of PES in θ and in poor solvents and to construct a diagram of states with variables (low molecular weight salt concentration and solvent quality) but also to calculate correlation functions of PES and moreover to obtain the contribution of the electrostatic interaction to the free energy of PES. Our investigation reveals some interesting effects, which seem to be common

for all PES. These include an oscillating regime of the screening of a test charge, the possibility of microphase separation of the PES into oppositely charged domains in a poor solvent, and the possibility of regions within the diagram of states, where electrostatic and van der Waals contributions to the free energy are of the same order of magnitude. The last result is used in ref 7 for the development of the statistical theory of polyelectrolyte complexes, consisting of oppositely charged polyions. The expression for the electrostatic contribution to the free energy can be also important in considering a collapse of charged polymer networks, properties of charged macromolecules with external constraints (in pores, tubes, etc.), and in other cases, where the free energy of charged macromolecules should be minimized.

In section II we discuss some general physical properties of weakly charged PES, which are essential for the further treatment and which show the necessity of understanding the fluctuational behavior of such systems. In section III the random phase approximation (RPA) for PES is developed, and the expressions for correlation functions, the screening potential of the test charge and electrostatic contribution to the free energy, are obtained. In section IV we consider properties of polymer systems, when all the electric charges of PES are turned off. This system is called the basic polymer system. Analysis of the basic polymer system will enable us to introduce the notion of
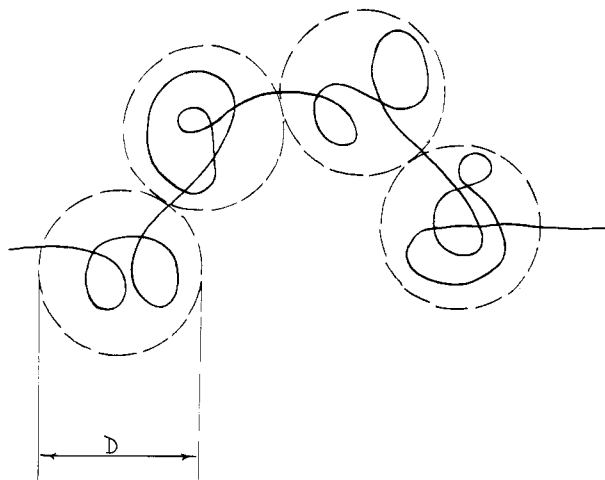
Figure 1. Polyelectrolyte conformation in a very dilute solution: the chain of electrostatic blobs.

the so-called induced electric charge. Then in section V we analyze the results obtained for simple PES and consider the diagram of states for the solution. Here the behavior of PES in a poor solvent and microphase separation are considered. Conclusions and discussions are given in section VI.

II. Physical Picture of Weakly Charged PES

Let us consider a polyelectrolyte molecule as a flexible filament, on which monomers are strung (the model "beads on a filament"[8] with Gaussian correlations between adjacent monomers and the mean-square distance a^2 between them. The interaction between the monomers is of van der Waals type and will be described by the corresponding virial coefficients. In the case of semidilute PES (the polymer volume fraction being small), it will be sufficient to use only the second virial coefficient $B = (v/2)(1 - 2\chi)$, where v is the excluded volume of monomers and χ is the Flory–Huggins parameter.[3]

The linear charge density of a polyelectrolyte molecule will be described by the parameter $m = eN/Q$, where Q is the total charge of the macromolecule, N is the degree of polymerization, and e is the electron charge. If $m \gg 1$ the macromolecule behaves as if two neighboring charges are separated by $(m - 1)$ uncharged monomers.

The difference between weakly and strongly charged polyelectrolytes is that in the former case the energy of the Coulomb interaction between adjacent charges on a chain is small in comparison with the temperature T, given in energy units: $u = e^2/\epsilon Ta \ll m^{1/2}$, where ϵ is the dielectric constant of the solvent, and in the latter case $u \gg m^{1/2}$.

It is well-known[1-5] that a single weakly charged polyelectrolyte molecule in a salt-free solution forms a rod of so-called "electrostatic blobs"—the chain fragments within which the energy of electrostatic interaction between charges is of the order of T (see Figure 1). (In such blobs Coulomb forces have only a minor influence on the local properties of a chain.)

In good solvents ($\chi < 1/2$) the blob size and the number of charges in it (p) are given by the following interpolation formulas:

$$D = \frac{am^{2/3}}{u^{1/3}}(1 + \zeta)^{2/7}; \qquad p = \frac{m^{1/3}}{u^{2/3}}(1 + \zeta)^{1/2} \qquad (1)$$

where $\zeta = Bm^{2/3}/(u^{1/3}a^3)$ is the excluded-volume parameter of the electrostatic blobs.[3] A blob is considered to be Gaussian if $\zeta \ll 1$ (ref 1) or swelled if $\zeta \gg 1$ (ref 2) (critical

indices are chosen in the Flory approximation[3]). In poor solvents ($\chi > 1/2$) a coil to globule phase transition occurs for each electrostatic blob, which leads to condensation of counterions (see ref 4).

When electrostatic blobs of different chains do not overlap, each blob can be considered as a single charged monomer,[4,5] since the Coulomb interaction energy between adjacent blobs is of the order T, and the chain of blobs represents a strongly charged polyelectrolyte. In this case the induced electrostatic persistence length should be taken into account.[9] The statistical theory of such systems was developed only for PES at high salt concentrations.[10] However, when the salt concentration decreases this theory encounters formidable difficulties.[11] Therefore the following treatment will be restricted to the region of monomer concentrations $\rho \gg \rho^*$, where ρ^* is the critical concentration when electrostatic blobs begin to overlap, which can be obtained from eq 1:

$$\rho^* = \frac{pm}{D^3} = \frac{u^{1/3}}{m^{2/3}a^3}(1 + \zeta)^{-5/7} \qquad (2)$$

In this concentration region the electrostatic energy is almost independent of the chain conformation due to the long-range nature of the Coulomb interaction. So its influence on the local properties of chains is negligible and its contribution to the free energy is determined by the collective behavior of PES. Systems of this type are naturally described by using the one loop or random phase approximation (RPA), known for electrolyte solution as the DH approximation.

It should be emphasized, however, that due to the polymeric nature of PES the Coulomb contribution to the free energy of a polyelectrolyte is quite different from the DH one.[11] Indeed, the presence of counterions makes the polyelectrolyte solution electroneutral, and so the electrostatic contribution is solely fluctuational, and should be determined by the correlation functions of the system. These functions are known to be quite different from the ideal gas ones (used in the DH theory[12]), so the electrostatic contribution to the free energy will also differ from that in the ideal gas case. Fluctuations in a polymer solution are known to be stronger than the ideal gas ones, and it will be shown below that the screening radius is usually smaller and the absolute value of the electrostatic contribution to the free energy is greater as compared with the DH case. The rigorous development of the RPA for PES will be performed in section III. Another important feature of PES is the possibility of a microphase separation in poor solvents, i.e., separation of the solution into oppositely charged microdomains rich and poor in polyions. Indeed, it is well-known[3] that in the absence of electrostatic interactions such a solution separates into two different macrophases poor and rich in polymer. However, in PES such separation leads to the appearance of a large unscreened electric charge, which must be neutralized, by redistribution of counterions. However, this is very unfavorable from the entropy point of view. Indeed, owing to the high degree of polymerization the translational entropy of each monomer of a macromolecule is negligible in comparison with the translational entropy of counterions. It is the existence of these two opposite tendencies which may lead under certain conditions to the formation of charged microdomains poor and rich in polyions. These conditions will be specified in section V.

III. Random Phase Approximation (RPA)

Assuming that the system under consideration is sufficiently uniform (otherwise, as will be shown below, the RPA would not be applicable), its statistical sum Z can

be represented as a functional integral over the smoothed densities $\{\rho_i(r)\}$ of particles of all types constituting the system[8]

$$Z = A \int \exp(-F(\{\rho\})/T)D\rho \qquad (3)$$

where $F(\{\rho_i\})$ is the free energy of PES as a function of a given generally speaking nonequilibrium density of particles of each sort $\{\rho_i(\vec{r})\}$ and A is a normalization constant. Owing to the difference between scales of the Coulomb and van der Waals interaction, $F(\{\rho_i\})$ can be represented as

$$F(\{\rho_i(\vec{r})\}) = F_b(\{\rho_i(\vec{r})\}) + U_{cl}(\{\rho_i(\vec{r})\}) \qquad (4)$$

where $U_{cl}(\{\rho_i(\vec{r})\})$ is the Coulomb interaction energy and $F(\{\rho_i(\vec{r})\})$ is the contribution to the free energy due to the short-range non-Coulomb interactions. $F_b(\{\rho_i(\vec{r})\})$ can be regarded as a free energy of a model system (basic polymer system) in which the polymer structure and the interaction between particles are the same as in PES under consideration with the exception that all charges of polyions and in the solution are set equal to zero.

If we take as variables of the functional integration the Fourier components of the deviation of the densities $\{\rho_i(\vec{r})\}$ from their corresponding equilibrium values N_i/V (N_i is the number of particles of type i; V is the volume of the system)

$$\rho_i(\vec{k}) = \sum_{j=1}^{N} \exp(i\vec{k}\vec{r}_j) - N_j$$

then

$$D\rho = \prod_{i=1}^{M} \prod_k d\rho_i(\vec{k})$$

and

$$U_{cl}(\{\rho\}) = 2\pi e^2 \int \frac{z_i \rho_i(\vec{k}) z_i \rho_i(-\vec{k}) \; d^3k}{\epsilon \vec{k}^2 (2\pi)^3} \qquad (5)$$

where z_i is the valency of ions of type i. Here and below (if not stated otherwise) summation is implied over repeated indices from 1 to M.

Representation (3) holds when charges situated at distances greater than the characteristic scale of smoothing give the major Coulomb contribution to Z. For a relatively homogeneous system, which can be treated with the RPA, this condition is always fulfilled.

According to the conventional approach[3,11,13] (which corresponds to the linearization of the response of the basic polymer system to the Coulomb interaction), the application of the RPA to a system implies that in the expansion of the free energy $F_b(\{\rho\})$ in density fluctuations only the first nonvanishing term is left

$$F_b(\{\rho\}) = F_0 + \frac{T}{2} \int \tilde{G}_{ij}^{-1}(\vec{k})\rho_i(\vec{k})\rho_j(-\vec{k})\frac{d^3k}{(2\pi)^3} \qquad (6)$$

where F_0 is the equilibrium density of the free energy of the basic polymer system (the term linear in $\rho_i(k)$ vanishes, because $\delta F_b(\{\rho\})/\delta\rho_i = \mu_i$ is a constant chemical potential of particles of type i and $\rho_i(0) = 0$) and $\tilde{G}_{ij}(k)$ is the matrix of correlation functions of the basic polymer system

$$\tilde{G}_{ij}(\vec{k}) = \langle \rho_i(\vec{k})\rho_j(-\vec{k})\rangle_b/V$$

where $\langle...\rangle_b$ means averaging over the basic polymer system with $F_b(\{\rho\})$ taken in the form (5). Combining eq 3–6, we obtain

$$G^{-1}_{ij}(\vec{k}) = \tilde{G}^{-1}_{ij}(\vec{k}) + \frac{4\pi e^2}{\epsilon T k^2}z_i z_j \qquad (7)$$

which leads to the following expression for the matrix of correlation functions of PES:

$$G_{ij}(\vec{k}) = \tilde{G}_{ij}(\vec{k}) - \frac{4\pi L \tilde{G}_{im}z_m \tilde{G}_{in}z_n}{k^2 + \kappa^2(k)} \qquad (8)$$

where $L = e^2/\epsilon T = ua$ is the Bjerrum length and

$$\kappa^2(k) = 4\pi L z_m \tilde{G}_{mn}z_n \qquad (9)$$

If the basic system contains no polymers, but only a low molecular weight electrolyte, then $\tilde{G}_{mn} = \|\rho_m\delta_{mn}\|$ and eq 7–9 reduce to the well-known DH results.[12]

From eq 8 it is easy to obtain the correlation function of the total charge density $\rho_q(r) = z_i\rho_i(r)$:

$$G_q(\vec{k}) = z_i z_j G_{ij}(\vec{k}) = \frac{k^2 \kappa^2(k)}{4\pi L(k^2 + \kappa^2(k))} \qquad (10)$$

Equation 10 enables us to obtain the general solution for the screening of a test charge. Indeed, a Fourier component of the screened potential of a test charge e_0 is

$$\psi(\vec{k}) = 4\pi(e_0 + \delta q(\vec{k}))/\epsilon k^2$$

where $\delta q(k)$ is the density of induced charges, readily obtained from

$$\delta q(\vec{k}) = - \frac{4\pi L e_0 G_q(\vec{k})}{k^2}$$

Thus using eq 10 we get

$$\psi(\vec{k}) = \frac{4\pi e_0}{k^2 + \kappa^2(k)} \qquad (11)$$

Equation 11 is a straightforward generalization of the Khokhlov and Khachaturian[5] results to multicomponent (heteropolymer) systems.

The free energy of PES $F = -T \ln Z$ can be obtained by substituting eq 4–6 into eq 3 and calculating the Gaussian functional integral. The normalization constant A can be fixed from the condition $Z = \exp(-F_0/T)$ in the absence of the Coulomb interaction and F_0 is the equilibrium free energy of the basic polymer system. Thus we have

$$F = F_0 + \Delta F_c = F_0 - T \ln \langle\exp(-U_{cl}/T)\rangle_b$$

Calculating the Gaussian integral (3) by standard methods (see, for example, ref 13), we get

$$\Delta F_c = \frac{VT}{2} \int \frac{d^3k}{(2\pi)^3} \ln (1 + \kappa^2(k)/k^2) \qquad (12)$$

It should be stressed that the validity of the RPA, i.e., the consideration of the functional integral (3) as the Gaussian one, is connected with the possibility of neglecting higher terms of the expansion of $F(\{\rho_i(k)\})$ in $\rho_i(k)$, omitted in eq 6. Thus, the RPA can be applied to relatively homogeneous systems, where fluctuations of densities are small enough. As discussed above the latter condition for PES corresponds to overlapping of electrostatic blobs (see eq 2) or to sufficiently high salt concentrations. More rigorous consideration of the RPA applicability is given in Appendix 1.

It follows from eq 8, 11, and 12 that for the further analysis of PES properties we need explicit expressions for correlation functions $\tilde{G}_{ij}(k)$ of the basic polymer system, which will be considered in detail in the next section.

IV. Basic Polymer System

Here and below we shall regard the basic polymer system as the semidilute solution ($N \to \infty$). Depending upon the

value of the parameter $\eta = B/a^3(B\rho)^{1/2}$ which was introduced by Edwards[13] (see also ref 14, 15), such a solution can be either in a weakly ($\eta \ll 1$, Edwards regime) or in a strongly ($\eta \gg 1$, scaling regime) fluctuating regime.[3] We shall first derive an expression for the correlation matrix of a multicomponent polymer solution at $\eta \ll 1$ and then generalize it to the case of a scaling solution. Thorough consideration of the case of $\eta \ll 1$ enables us to study the interplay between Coulomb and non-Coulomb interactions and to define the concept of so-called induced monomer charge.

A. Correlation Functions in the RPA. Correlation functions of the semidilute solution of linear macromolecules in the RPA were calculated for the first time by Edwards[13] and for the mixtures of flexible macromolecules with arbitrary structures by one of us.[14]

In ref 14 the following trick of Lifshitz[16] was used: when the ratio $v/a^3 \gg 1$, the free energy $F_b(\{\rho_i(\vec{r})\})$ of the basic polymer system can be divided into two parts:

$$F_b(\{\rho\}) = -TS_{\text{conf}}(\{\rho\}) + E(\{\rho\}) \qquad (13)$$

The first term in eq 13 is the configurational entropy of the basic polymer system, which includes also the energy of chemical bonding of monomers in macromolecules, and the second term is the energy of so-called volume interaction. In order to obtain an explicit expression for the second term, Lifshitz introduced the notion of the "system of separate monomers" (SSM). The SSM is equivalent to the original basic polymer system, but all chemical links between monomers are considered to be broken. The SSM represents a gas (liquid) of monomers without linear memory.[8,13,15]

Moreover, it was shown[8] that $E(\{\rho\})$ is the same for the basic polymer system and for the corresponding SSM (more precisely this is true when $v/a^3 \ll 1$ and is valid only qualitatively when $v \simeq a^3$). Using equations 6 and 13, one can show that the matrix of correlation functions equals

$$\tilde{G}^{-1}{}_{ij}(\vec{k}) = \frac{\delta^2 F_b}{T\delta\rho_i(\vec{k})\delta\rho_j(-\vec{k})} = g^{-1}{}_{ij}(\vec{k}) - c_{ij}(\vec{k}) \qquad (14)$$

where $g_{ij}(\vec{k}) = -\delta^2 S_{\text{conf}}/\delta\rho_i(\vec{k})\delta\rho_j(-\vec{k})$ is the so-called structure matrix of the basic polymer system,[14] which has the meaning of its matrix of correlation functions in the absence of volume interaction, and $c_{ij}(\vec{k}) = \delta^2 E(\{\rho\})/\delta\rho_i(\vec{k})\cdot\delta\rho_j(-\vec{k})$ is the matrix of direct correlation functions of the SSM, which is well-known in the theory of liquids.[17]

Using eq 14, we can separate short-range interaction of the SSM from the long-range polymer effects. Indeed $\tilde{G}_{ij}(k)$ can be represented in several equivalent ways:[14]

$$\tilde{G}(k) = (g(k) - c(k))^{-1} =$$
$$G_{\text{SSM}} + (E + \rho h)(J^{-1} - h)^{-1}(E + \rho h) \qquad (15)$$

where matrix $E = \|\delta_{ij}\|$, $\rho = \|\rho_i\delta_{ij}\|$, the matrices c, $G_{\text{SSM}} = (\rho^{-1} - c)^{-1}$, and $h = (c^{-1} - \rho)^{-1}$ characterize fluctuational properties of the SSM, and the structure matrix of polymer solution equals $g(k) = \rho + J(k)$ with

$$J(k) = \|\sum_s n_s \langle \exp[ik(r(l_i) - r(l_j))]\rangle_s\|_{ij} =$$

$$\|\sum_s n_s \sum_{p=1}^{\infty} \nu_{ij}{}^s(p)g(k)^p\|_{ij} \qquad (16)$$

In eq 16 $\langle ...\rangle_s$ means averaging over all configurations of a macromolecule with the structure of type s, $r(l_i)$ is the radius vector of any of its monomer of type i, and n_s is the number of macromolecules of type s in an unit volume. Summation should be performed first over all pairs of monomers of type i and j of a macromolecule of type s and then over all types of macromolecules. $\nu^s{}_{ij}(p)$ is the number

of corresponding pairs of monomers separated by p links. For the model of "beads on a filament",[8] $g(k) = \exp[-(k^2a^2)/6]$.

Equation 15 facilitates substantially the calculation of the correlation functions in eq 14. We are interested in the region where $ka \ll 1$, and therefore all the parameters of the SSM can be considered as independent of k and equal to their values at $k = 0$. Using eq 15, we can also avoid another difficulty, encountered in multicomponent systems, namely, the consideration of correlation matrices of the high order. Really, as can be seen from eq 16, any element of $\|J\|$ equals to zero when at least one of its indexes corresponds not to a polymer but to a low molecular weight component.

Combining eq 15, 16, and 19 we obtain

$$\kappa^2(k) = \kappa_s{}^2(k) + \kappa_p{}^2(k) \qquad (17)$$

where $\kappa_s{}^2(k) = 4\pi L z_i z_j G_{\text{SSM}}(k)_{ij}$ is the parameter describing the screening of the electrostatic interaction by low molecular weight components of the SSM and counterions. Specific polymer screening is described by the parameter

$$\kappa_p{}^2(k) = 4\pi L z_i*(J^{-1}(k) - h)^{-1}{}_{ij}z*{}_j \qquad (18)$$

where $z*_i$ is the effective valency:

$$z*_i = z_i + \sum_{j=1}^{M} h_{ij}\rho_j z_j = z_i + \tilde{z}_i \qquad (19)$$

The valency $z*_j$ equals the sum of the bare valency z_i and the so-called induced valency $\tilde{z}_i$, which is induced by van der Waals interaction (i.e., by selective adsorption of charges on monomers).

Expressions for $\kappa_s{}^2$ and $\kappa_p{}^2$ can be most readily obtained for a weakly charged polyelectrolyte with the random distribution of charges along chains. Suppose that $W_1 = 1/m$ is the probability for any monomer to have the charge e ($z = 1$), then $W_0 = 1 - 1/m$ is the probability for a monomer to be neutral. Owing to the statistical independence of the ionization of a monomer, $\nu_{ij}(p)$, introduced in ref 16, takes the form $\nu_{ij}(p) = W_i W_j \nu(p)$, where i or j can correspond either to W_1 or to W_0 and $\nu(p)$ is the number of pairs of monomers (both ionized and neutral) separated by p links. Thus we can use eq 17–19 and consider a polymer to contain monomers of the same type with the mean charge e/m.

The expression for $J(k)$ in a homopolymer case is well-known.[3,13] Using eq 16 we have

$$J(k) = \frac{12\rho}{k^2a^2} \qquad (20)$$

where ρ is the monomer concentration. This expression is asymptotically precise when $ka \ll 1 \le kR$ (R is the mean radius of gyration of a polymer chain). And for $kR \ge 1$ eq 20 is the more precise the closer the molecular mass distribution in the solution is to the Flory type one.[14,18] When the volume fraction in the solution is small, the expression for $h(k) = h(0)$ (see notations to eq 15) can be easily obtained:

$$h(0) = -2B - 3B_3\rho \qquad (21)$$

where B_3 is the third virial coefficient of monomer-monomer interaction. In this paper we neglect for simplicity all the nonelectrostatic interactions in the solution except for that between monomers. Then from eq 15, 20, and 21 we obtain the monomer-monomer correlation function

$$G_E(k) = \frac{12\rho\xi_E{}^2/a^2}{k^2\xi_E{}^2 + 1} \qquad (22)$$

where index E refers to the polymer solution in Edwards regime ($\eta \ll 1$) and ξ_E is the corresponding correlation radius:

$$\xi_E = a/(-12\rho h)^{1/2} = a/(24B\rho)^{1/2} \qquad (23)$$

Thus the contribution of the SSM to $\kappa^2(k)$ is

$$\kappa_s^2(k) = 12I_s/a^2 \qquad (24)$$

where

$$I_s = \frac{\pi L a^2}{3}(c_i z_i^2 + 2\rho/m) \qquad (25)$$

and c_i and z_i are the concentrations and valences of salt ions of type i, respectively. The polymeric contribution to the screening can be obtained from eq 9, 18, and 22:

$$\kappa_p^2(k) = \frac{12I_p}{a^2(k^2a^2/12 - h\rho)} \qquad (26)$$

where

$$I_p = \pi L \rho a^2/(3m^2) \qquad (27)$$

Though the results (24–27) were obtained under the assumption that the distribution of charges along the chain is statistically independent, they are not limited to this case. Indeed, when the correlation between adjacent charges is of a short-range type, these results are also correct provided that the quantities v, a, and χ refer to quasi-monomers.[8] The opposite case of the long-range correlations, arising from a particular chemical structure of a macromolecule, can be treated by using a proper structure matrix of the system. Finally, nonelectrostatic interactions of a polymer with salt and counterions can be also accounted for by the introduction of an induced monomer charge (see above). Interaction of this type can lead to the interesting polymer–salt effects, e.g., neutral macromolecules will behave as weakly charged, owing to the interaction with salt.

B. Correlation Functions in the Scaling Regime. B1. Moderate Salt Concentrations. Equations 24–27 for the screening parameter $\kappa^2(k)$ have been obtained for the basic polymer system being in the Edwards regime ($\eta \ll 1$). They can be generalized to the scaling case ($\eta \gg 1$), if the characteristic radius of screening is larger than the correlation radius of the solution, which is true at moderate salt concentrations (see section IV). Indeed, the monomer correlation function in a semidilute scaling solution $G_{sc}(k)$ at $k\xi_s \ll 1$ can be approximated[3] by

$$G_{sc}(k) = \frac{\rho^2 \xi_s^3}{k^2 \xi_s^2 + 1} \qquad (28)$$

where

$$\xi_s \cong (a/(B\rho)^{1/2})\eta^{1/2} \qquad (29)$$

is the correlation radius of the scaling solution which is defined to a precision of a constant numerical multiplier. Besides the polymer contribution to screening, there is also a contribution from the system of separate charges, which is evidently determined by the same equations, (24) and (25). It can be seen from eq 9, 17, 28, and 29 that polymer contribution $\kappa_p^2(k)$ is determined by eq 26 and 27 in which I_p and h should be substituted by the interpolation formulas

$$I^*_p = I_p/(1 + \eta)^{1/2}; \qquad h^* = h/(1 + \eta) \qquad (30)$$

and for the correlation radius of the basic polymer solution

$$\xi = \xi_E(1 + \eta)^{1/2} \qquad (31)$$

When $\eta \ll 1$, eq 30 and 31 give eq 23, 26, and 27 and when $\eta \gg 1$ they give the corresponding scaling dependencies.[28,29] Henceforth we shall omit asterisks in parameters I^*_p and h^*, the interpolation dependencies (30) and (31) being implied.

B2. High Salt Concentrations. If the characteristic radius of screening by salt r_s (see eq 36) is smaller than the correlation radius of the solution, specific polymer contribution to the screening is determined by distances at which the correlation function $G_{sc}(k)$ is no longer described by eq 28 (for $k\xi_s \sim 1$) and the scaling expression (obtained by Edwards, see ref 3) should be used:

$$G_{sc}(k) \cong \rho^2 \xi_s^{4/3}/k^{5/3} \qquad (32)$$

where critical indices are taken in the Flory approximation.[3] In this case, from eq 9 we get

$$\kappa_p^2(k) \cong L\rho^2 \xi_s^{4/3}/(m^2 k^{5/3}) \qquad (32a)$$

This region of concentrations will not be examined in more detail further. However, some additional results can be found in Appendix 2.

V. Diagram of States

Now we can consider the diagram of states for a weakly charged polyelectrolyte solution. For convenience we shall introduce a characteristic scale of screening in a saltless polyelectrolyte solution:

$$r_0 = \frac{a}{(144I_p)^{1/4}} = a\left(\frac{m^2(1 + \eta)^{1/2}}{48\pi u\rho a^3}\right)^{1/4} \qquad (33)$$

Choosing r_0 as a length scale, we obtain in dimensionless units

$$\kappa^2(k) = s + \frac{1}{x^2 + t} \qquad (34)$$

where $x = |\vec{k}|r_0$ is the dimensionless wave vector

$$s = \frac{I_s}{I_p^{1/2}} = \frac{r_0^2}{r_s^2}; \qquad t = -\frac{h}{I_p^{1/2}} = \frac{r_0^2}{\xi^2} \qquad (35)$$

and

$$r_s = a\{4\pi u a^3(c_i z_i^2 + 2\rho/m)\}^{-1/2} \qquad (36)$$

is the radius of the DH screening by salt and the system of separate charges.[9] The variables s and t which can be called the reduced salt concentration and the reduced solvent quality are useful for the description of weakly charged polyelectrolyte solutions.

A. Microphase Separation. To consider the thermodynamic stability of polyelectrolyte solution, we start with analysis of the correlation function of the total charge $G_q(k)$ (see eq 10) or the correlation function of monomer–monomer concentrations $G_\rho(k)$ (see eq 8). If $G_q(k)$ or $G_\rho(k)$ are positive for all values of k, then a spatially homogeneous state of polyelectrolyte solution will be stable. Boundaries of thermodynamic stability of this state (spinodal) are determined by the equation[19,20]

$$\min G_q^{-1}(k) = 0 \quad \text{or} \quad \min G_\rho^{-1}(k) = 0 \qquad (37)$$

where $G_q^{-1}(k)$ is minimized with respect to all k. If the solution of eq 37 corresponds to $k_0 = 0$, then the usual phase separation into macroscopic phases rich and poor in polymer will take place. If eq 37 has a solution for $k_0 \neq 0$, the microphase separation will occur.[19,20] The value k_0^{-1} is the characteristic scale of the microphase separation.

From eq 10, 34, and 35, we obtain in dimensionless units

$$G_q(x) = \frac{1}{4\pi L r_0^2} \frac{x^2[s(x^2 + t) + 1]}{(x^2 + s)(x^2 + t) + 1} \quad (38)$$

and from eq 8, 22, 34, and 35

$$G_\rho(x) = \frac{1}{4\pi L r_0^2} \frac{x^2 + s}{(x^2 + t)(x^2 + s) + 1} \quad (39)$$

It can be easily seen that $G_q^{-1}(x)$ and $G_\rho^{-1}(x)$ exhibit strong dependencies on s. For each $s \leq 1$, eq 37 is fulfilled for

$$t_* = s - 2; \quad x_* = 1 - s = -1 - t; \quad k_* = \frac{(1 - s)^{1/2}}{r_0} \quad (40)$$

and thus the microphase separation takes place on the oppositely charged microdomains rich and poor in polymer.

When $s > 1$ the behavior of $G_q(x)$ depends on the sign of $y = 1 + st$. If $y > 0$, $G_q(x)$ will be positive for all $x^2 \geq 0$ and the polyelectrolyte system will be stable (or at least metastable). If $y \leq 0$, then for $x^2 = -(1 + st)/s$ this function will have an infinite gap and in a certain interval of a wave vector values the function will be negative, and thus the spatially homogeneous state will be absolutely unstable with respect to the corresponding fluctuations. Therefore, when $s \gg 1$ the microphase separation will be transformed into the usual separation in two macroscopic phases and the spinodal equation will have the form

$$t_* = -1/s \quad (41)$$

Equation 41 can be rewritten with more common notations:

$$B_{eff} = B + \frac{1}{2m^2(c_i z_i^2 + 2\rho/m)} = 0$$

The effective virial coefficient B_{eff} has the form obtained earlier by Flory.[18] Thus at high salt concentrations ($s \gg 1$) the condition for the phase separation is $B_{eff} = 0$ (instead of $B = 0$).

B. Microdomain Structure of the Polyelectrolyte Solution. The structure of a weakly charged polyelectrolyte solution after microphase separation can be found out by means of the well-known Landau expansion of the free energy of the spatially inhomogeneous state of the system[12,19–21] over $\delta\rho(\vec{k})$ (Fourier components of the deviation of the monomer concentration from the equilibrium value) up to the fourth order:

$$\frac{F(\{\rho\}) - F_0}{T} = \frac{1}{2} \int G_\rho^{-1}(\vec{k})\delta\rho(\vec{k})\delta\rho(-\vec{k})\frac{d^3k}{(2\pi)^3} +$$

$$\frac{1}{3!} \int \Gamma_\rho^{(3)}(\vec{k}_1,\vec{k}_2,\vec{k}_3)\delta(\vec{k}_1+\vec{k}_2+\vec{k}_3)\prod_{i=1}^{3}\left[\frac{\delta\rho(\vec{k}_i)\,dk_i}{(2\pi)^3}\right] +$$

$$\frac{1}{4!} \int \Gamma_\rho^{(4)}(\vec{k}_1,\vec{k}_2,\vec{k}_3,\vec{k}_4)\delta(\vec{k}_1+\vec{k}_2+\vec{k}_3+\vec{k}_4)\prod_{i=1}^{4}\left[\frac{\delta\rho(\vec{k}_i)\,dk_i}{(2\pi)^3}\right] \quad (42)$$

An expression for $G_\rho^{-1}(k)$ was obtained earlier (see eq 39). Expressions for $\Gamma_\rho^{(3)}$ and $\Gamma_\rho^{(4)}$ have the form (to within $1/N$)[19]

$$\Gamma_\rho^{(3)}(\vec{k}_1,\vec{k}_2,\vec{k}_3) = -\frac{(\vec{k}_1^2 + \vec{k}_2^2 + \vec{k}_3^2)a^2}{24\rho^2}$$

$$\Gamma_\rho^{(4)}(\vec{k}_1,\vec{k}_2,\vec{k}_3,\vec{k}_4) = \frac{(\vec{k}_1^2 + \vec{k}_2^2 + \vec{k}_3^2 + \vec{k}_4^2)a^2}{12\rho^3} \quad (43)$$
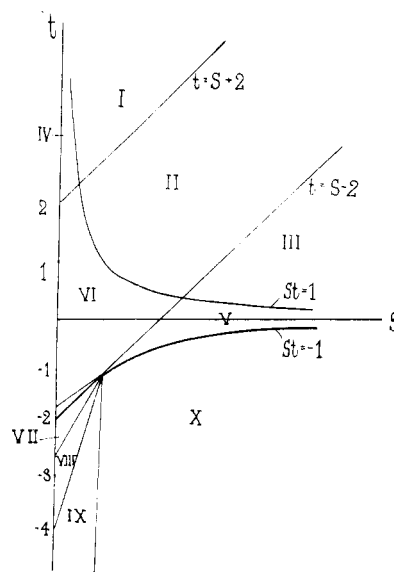
Figure 2. Diagram of states for the solution of weakly charged polyelectrolytes. Thick line is spinodal; I–VI are different fluctuation regions; VII is a bcc lattice; VIII is a two-dimensional hexagonal lattice; IX is a lamelar structure; X corresponds to the separation of two phases.

We are interested in the expansion (42) only as far as fluctuations near $k = k_*$, $t = t_*$ are concerned (see eq 42). So expanding eq 42 in the vicinity of this point we obtain

$$\frac{r_0^2\Delta F}{Va^2T(1 - s)} = \frac{1}{6}\left[\frac{\Delta t}{4(1 - s)} + (\vec{x} - \vec{x}^*)^2\right]\sum_{\vec{x}}\varphi_{\vec{x}}\varphi_{-\vec{x}} -$$

$$\frac{1}{48}\sum_{\vec{x}_1+\vec{x}_2+\vec{x}_3}\varphi_{\vec{x}_1}\varphi_{\vec{x}_2}\varphi_{\vec{x}_3} + \frac{1}{72}\sum_{\vec{x}_1+\vec{x}_2+\vec{x}_3+\vec{x}_4}\varphi_{\vec{x}_1}\varphi_{\vec{x}_2}\varphi_{\vec{x}_3}\varphi_{\vec{x}_4} \quad (44)$$

where $\varphi_{\vec{x}} = \delta\rho(\vec{x})/\rho V$, x is the dimensionless wave vector $\Delta t = t - t_*$, and $\Delta F = F(\{\rho\}) - F_0$.

If expression 44 were exact, then following ref 19 and 21 we would get the phase structure of the PES in the region of a poor solvent ($t < 0$) shown in Figure 2. Indeed in this case as was shown in ref 21 in the region VII, VIII, and IX, the system would have the symmetry of a body-centered cubic (bcc) lattice, a two-dimensional hexagonal lattice, and one-dimensional lamelar structure, respectively, with the first-order phase transitions from one symmetry to another.

However, we do not present the rigorous expressions for the phase transition lines, because eq 44 is just approximate: in the vicinity of the expansion point all its terms (and not only four of them) are the same order of magnitude. Nevertheless the phase diagram (Figure 2) seems to be correct at least qualitatively. The phase transition lines are described by the general dependencies: $\Delta t \simeq (1 - s)$. For a block copolymer case, considered by Leibler,[19] the φ^3 term had an additional small parameter owing to which borders of the phase diagram, in contrast to our case, could be determined quantitatively.

Microphase separation can occur only when $s \ll 1$, which with the help of eq 35 (with $c_i = 0$) transforms to an equivalent condition $\rho L a^2 \ll 1$. Therefore microphase separation can be observed only for moderate concentrations of monomers. For example, it is unlikely to occur in weakly charged polyelectrolyte melts.

Expansions (42) and (44) are valid only sufficiently far from the spinodal ($\Delta t = 0$). The region near the spinodal, where fluctuations of the order parameter $\delta\rho(k)$ are strong and RPA is violated, can be estimated by using results of ref 22 (see Appendix 1), to be $|\Delta t| \ll [(1 - s)/(\rho a^2 r_0)^2]^{1/3}$. It can be seen that the RPA can be used sufficiently far

from the point $s = 1$, and $\rho a^2 r_0$ is the Ginzburg number of our problem.[12] But it is easy to notice that $\rho a^2 r_0 = (\rho/\rho^*)^{3/4} \gg 1$, where ρ_* is the concentration of the overlap of electrostatic blobs (see eq 2), and $\rho \gg \rho_*$ is the condition of applicability of the RPA. So the fluctuation region near the spinodal is rather small. The RPA fails near $s = 1$, $t = -1$.

C. Different Fluctuation Regimes of the Diagram of States. 1. Contribution of the Coulomb Interaction to the Free Energy of a Polyelectrolyte Solution.
Using eq 12, 13, and 17-21, we can calculate now the contribution ΔF_c of the Coulomb interaction to the free energy of PES. It is easy to note that the integral (13) diverges at large k. However, this divergency is connected with the infinite self-energy of charges. This self-energy should be subtracted from the integral as it is in the DH theory.[12] Then we obtain the convergent integral and the integration gives

$$\Delta F_c = \Delta F_E + \Delta F_{RPA} \qquad (45)$$

where

$$\Delta F_E = \frac{VTt^{3/2}}{12\pi r_0^3} = \frac{VT}{12\pi \xi^3} \qquad (46)$$

and

$$\Delta F_{RPA} = \frac{VT}{12\pi r_0^3}[(1 + st)^{1/2} - s - t][s + t + 2(1 + st)^{1/2}]^{1/2} \qquad (47)$$

The total free energy of PES F consists of ΔF_c and F_0 (see eq 12), where F_0 is the free energy of the basic polymer solution. In the mean-field approximation F_0 is determined by the thermodynamics of the system of separate monomers and for simplicity it can be chosen in the Flory-Huggins form F_{FH}.[3,18] In the RPA, $F_0 = F_{FH} + \Delta F_{RPA}^{(0)}$, where $\Delta F_{RPA}^{(0)}$ is the one loop correction to the mean-field approximation that was calculated by Edwards.[13] It can be easily seen[13] that $\Delta F_{RPA}^{(0)} = -\Delta F_E$, so that the total free energy of the polyelectrolyte solution is

$$F = F_{FH} + \Delta F_{RPA} \qquad (48)$$

Thus ΔF_{RPA} is the total one loop correction to the mean-field approximation that includes corrections due to both Coulomb and short-range excluded-volume interactions.

It is interesting to note that the final result does not contain the correction $\Delta F_E \simeq t^{3/2}$, which in a poor solvent ($B < 0$, $t < 0$) is senseless. The absence of this term in eq 48 reflects the stability of the PES in poor solvents (see above).

For the basic polymer system in the scaling regime $F_0 \simeq VT/\xi^3$.[3] F_0 is of the same order of magnitude as ΔF_E. Therefore, taking into account that scaling laws are determined to a precision of a numerical constant, we obtain the total free energy of a scaling semidilute polyelectrolyte solution

$$F = \Delta F_E + \Delta F_{RPA} = \Delta F_c \qquad (49)$$

Now that F is calculated, all thermodynamic characteristics of the solution can be obtained. Here we shall consider only the osmotic pressure ΔP.

For the weakly fluctuating basic polymer system ($\eta \ll 1$), the osmotic pressure of PES is

$$P = \frac{\partial F}{\partial V} = T\sum_i c_i + TB\rho^2 + \Delta P_{RPA} \qquad (50)$$

where the contribution of the polymer translational entropy is neglected and only the terms of the second order

in ρ are left, and then the contribution of the RPA correction to P has a fairly simple form:

$$\Delta P_{RPA} = -\frac{T}{24\pi r_0^3} \frac{[s + t + 2(1 + st)^{1/2}]^2 + 3(s - t)^2}{[s + t + 2(1 + st)^{1/2}]^{1/2}} \qquad (51)$$

When $\eta \gg 1$ or the third virial coefficient $B_3 \neq 0$ the expression for ΔP_{RPA} will be more complicated, but eq 51 reveals the asymptotic behaviors with respect to s and t.

2. Screened Potential of a Test Charge.
Physical interpretation of r_0, s, and t is revealed by consideration of the screening of a test electric charge e_0 in a polyelectrolyte solution. In accordance with eq 11 the expression for a screened Coulomb potential has the form

$$\psi(r) = \frac{4\pi e_0}{\epsilon} \int \frac{\exp(-i\vec{k}\vec{r})}{k^2 + \kappa^2(k)} \frac{d^3k}{(2\pi)^3}$$

This integral can be easily calculated by using eq 34 for $\kappa^2(k)$. Depending on the values of s and t, $\psi(r)$ can be either an oscillating or a nonoscillating function. Indeed, for $|s - t| \leq 2$

$$\psi(r) = \frac{e_0}{\epsilon r} \exp(-r/\lambda_e) \frac{\sin(r/\lambda_s + \alpha)}{\sin(\alpha)} \qquad (52)$$

where $\cot(\alpha) = (t - s)/[4 - (s - t)^2]^{1/2}$ with scales of screening

$$\lambda_e = \frac{2r_0}{[s + t + 2(1 + st)^{1/2}]}; \quad \lambda_s = \frac{2r_0}{[2(1 + st)^{1/2} - s - t]} \qquad (53)$$

For $|s - t| > 2$ we get

$$\psi(r) = \frac{e_0}{2\epsilon r}[\exp(-r/\lambda_e^-)[1 + \coth(\alpha)] + \exp(-r/\lambda_e^+)[1 - \coth(\alpha)] \qquad (54)$$

where $\coth(\alpha) = (t - s)/[(s - t)^2 - 4]^{1/2}$ with scales of screening

$$\lambda_e^\pm = \frac{2^{1/2}r_0}{\{s + t \pm [(s - t)^2 - 4]^{1/2}\}^{1/2}} \qquad (55)$$

In the vicinity of θ-point ($s \simeq 0$, $t \simeq 0$) the potential of the test electric charge oscillates with scales $\lambda_e \simeq \lambda_s \simeq 2^{1/2}r_0$. Thus r_0 is the characteristic scale of screening of Coulomb interaction by ideal Gaussian chains. Taking into account that r_s (see eq 36) is the radius of screening by salt and separate charges of a polymer, we can interpret s and t as the ratios of specific polymer radius of screening to a low molecular weight one or to the correlation radius of the basic polymer system, respectively. The regions of different regimes of screening, corresponding to different values of s and t are shown in Figure 2.

3. Different Asymptotic Expressions and Physical Interpretation.
The region $t \geq 0$ of the diagram corresponds to the stable basic polymer system, the line $t = 0$ being its spinodal. It has been shown in section V.A that PES is stable up to $t_* = s - 2$ if $s \leq 1$ and up to $t_* = -1/s$ if $s \geq 1$. Other characteristic lines in the s/t plane are $|s - t| = 2$, on which the regime of screening changes, and the crossover line $st = 1$, where asymptotics for the thermodynamic quantities are changed. These lines divide the s/t plane into different regions, where simple asymptotic expressions can be obtained.

First consider regions I-III, where $st \gg 1$ and the concentration of a polyelectrolyte or salt is sufficiently high. In this case the screening and electrostatic contribution to P will be evidently similar to the DH case.[12] Indeed,

from eq 55 we get for the screening radii in region I asymptotic expressions

$$\lambda_e^+ = r_0/t^{1/2} = \xi; \qquad \lambda_e^- = r_0/s^{1/2} = r_s \qquad (56)$$

and in region III the corresponding expressions can be obtained from eq (56) by interchanging s and t

$$\lambda_e^+ = r_0/s^{1/2}; \qquad \lambda_e^- = r_0/t^{1/2} \qquad (57)$$

Thus there are only two characteristic scales in this region: the correlation radius of the basic polymer solution ξ, and the radius of the DH screening by the system of separate charges r_s. In region I $\xi \leq r_s$ and in region III $\xi \geq r_s$. Screened potential of the test electric charge in this region (see eq 54) consists of two terms. In region I where $(t - s) \gg 2$ and coth $(\alpha) = 1 + 2/(t - s)^2$ the first term with $\lambda_e^- = r_s$ dominates, while the second term with $\lambda_e^+ = \xi$ gives only a minor correction to screening. In contrast, in region III, where $(s - t) \gg 2$ and coth $(\alpha) = -1 - 2/(t - s)^2$, the term with $\lambda_e^+ = r_s$ is dominant. But the long-range asymptotic of $\psi(r)$ $(r_s \ll r)$ has the form

$$\psi(r) = -e_0 \exp(-r/\lambda_e^-)/[\epsilon r(s - t)^2] \qquad (58)$$

Thus in this case fluctuations of a polymer solution lead to an apparent change of the sign of the test charge. In region II potential $\psi(r)$ (see eq 52) oscillates. But from eq 53 $\lambda_s = 2r_0 s^{1/2} \gg \lambda_e = r_0/s^{1/2} = r_s \simeq \xi$. Therefore when the sign of the screened potential changes, its amplitude becomes exponentially small and is difficult to observe.

The character of screening changes along the line $|s - t| = 2$, eq 52 and 54, for $\psi(r)$ being transformed continuously one into the other. Screening radii at boundaries $|s - t| = 2$ are $\lambda_s = \infty$, $\lambda_e = \lambda_e^+ = \lambda_e^-$.

The Coulomb contribution to the osmotic pressure ΔP_{RPA} in region I can be obtained in the form

$$\Delta P_{RPA} = \frac{T}{24\pi r_0^3}\left[s^{3/2} + t^{3/2} + \frac{3}{2t^{1/2}} \right] \qquad (59)$$

ΔP_{RPA} in region III can be obtained from eq 59 by interchanging s and t. The first term in eq 59 is the usual DH expression for the fluctuational Coulomb contribution of the system of separate charges,[12] the second correction due to the volume interaction was calculated by Edwards,[13] and the last term plays the dominant role in regions IV and V and will be considered later. Thus in regions I–III thermodynamic properties of the solution almost coincide with the DH ones.[12]

An entirely different situation is observed in regions IV and V, where $|st| \ll 1$. In region IV $(t \gg s)$ eq 55 gives

$$\lambda_e^+ = r_0/t^{1/2} = \xi; \qquad \lambda_e^- = r_0 t^{1/2} = r_0^2/\xi \gg \xi \quad (60)$$

and in region V $(s \gg t)$

$$\lambda_e^+ = r_0/s^{1/2} = r_s; \qquad \lambda_e^- = r_0 s^{1/2} = r_0^2/r_s \gg r_s \qquad (61)$$

In region IV, ΔP_{RPA} equals (see eq 51)

$$\Delta P_{RPA} = \frac{T}{24\pi r_0^3}\left[t^{3/2} + \frac{3}{2t^{1/2}} \right] \qquad (62)$$

and in region V it can be obtained from eq 62 by interchanging s and t. In region IV similar to the case of region I, the effective screening radius is λ_e^- (see eq 60), and in region V, similar to the case of region III, the apparent change of the sign of a test electric charge takes place if $r \gg r_s$ (see eq 58). Moreover, at the boundary of region V $(st = -1)$ the Coulomb interaction is not screened $(\lambda_e^- = \infty)$. This fact indicates instability of the system to phase separation.

Expressions 60–62 have a simple physical interpretation. In region IV the influence of the salt on screening is practically negligible and the screening can be described by the DH theory. In this case, however, the fragments of chain containing $M = 12\xi^2/a^2$ monomers should be considered as the screening object. In fact the radius of this screening object is of order ξ and is much smaller than $\lambda_e^- = r_0^2/\xi$ (see eq 60). Thus expression 60 for λ_e^- can be obtained from the DH expression for the screening radius (see eq 36) where eM/m is substituted for e and ρ/M for ρ/m. The second term in eq 62 is the contribution of self-interaction energy of these screening objects. Indeed self-energy of an object is $M^2 e^2/(\epsilon m^2 \xi)$, and there are $1/M$ objects in the unit volume, which finally gives eq 62.

In region V where all excluded-volume effects can be practically neglected, the remaining Coulomb interaction is of great importance (see eq 58). The screening of this interaction obeys the DH theory with screening objects being the fragments of the chain which contain $M = 12r_s^2/a^2$ monomers. The dimension of these screening objects r_s is much smaller than the screening radius $\lambda_e^- = r_0^2/r_s$ (see eq 61). Equation 61 for λ_e^- can be obtained in analogy with region IV, by using DH expression for the screening objects defined above. Similar to the case of region IV, the corrections to the osmotic pressure in region V are associated with the self-energy of the screening objects.

Still more evident entirely polymeric effects are revealed in region VI. Expressions 46 and 51–53 show that the potential of the test electric charge is oscillating at the boundary $t_* = -2 + s$; $s \leq 1$. Here $\lambda_e = \infty$ and the potential oscillates without screening. This fact reflects instability of the PES with respect to microphase separation. It is interesting to note that at the point $s = 1$, $t = -1$, $\lambda_e = \infty$, and $\lambda_s = \infty$ (see eq 53) the Coulomb potential interaction is completely unscreened.

By using eq 33, 35, and 36 it is easy to transform s and t variables into ρ and T ones. It can be shown that for a weakly fluctuating basic polymer system $(\eta \ll 1)$ with negligible triple collisions $(B_3 = 0)$ the isotherm $T = $ constant reduces to a ray:

$$s/t = \pi u^{2/3}/(3m^{1/3}\zeta) + \pi u c_i z_i^2/(6B\rho)$$

If $B_3 \neq 0$ or $\eta \gg 1$ the expression for the isotherm will be more complicated.

Surely the RPA cannot be used for all values of s and t. It is shown in Appendix 1 and section III that the RPA is valid when either $\rho > \rho_*$ or $r_s < D$ $(t > 0)$. It can be also shown that for $\zeta \ll 1$ these conditions are equivalent to $s \gg s_* = u^{2/3}/m^{1/3}$ and $t \gg \zeta$ and in the scaling region $\zeta \gg 1$ or $\eta \gg 1$ to $s \gg 1$ and $t \gg 1$ (in fact for $\rho = \rho_*$ the parameter $\eta = \zeta^{1/2}(1 + \zeta)^{5/14}$ and if $\zeta \gg 1$ then $\eta \gg 1$). Since polyions are weakly charged, $s_* \ll 1$ and for $\zeta \ll 1$, the RPA is valid practically for all values of s and t. For $\zeta \gg 1$ the RPA fails in region VI. If $t < 0$ only a small vicinity near spinodal should be excluded (see Appendix 1). The asymptotic expressions for the screening radii and ΔP obtained above can be adjusted for the scaling regimes in regions I, II, and IV (i.e., for $r_s \leq \xi$ or $s < t$), by using the interpolations (30 and 31). In regions III and V the concentration of salt is rather high and the proper accounting of properties of the scaling basic polymer system is necessary. This is done in Appendix 2.

Consideration of the electrostatic interaction contribution to the osmotic pressure reveals an interesting specifically polymeric effect. It is well-known that for a low molecular weight salt solution the RPA can be applied when the contribution ΔP_{RPA} to the full osmotic pressure is small.[12] This condition follows from the fact that the

major contribution to the osmotic pressure arises from the translational entropy of ions. A high degree of polymerization results in a negligibly small contribution from these degrees of freedom. However, such a minor contribution does not contradict the RPA applicability, which implies only small higher order corrections in comparison with the RPA one, but not a small RPA correction in comparison with the mean-field contribution.

It can be seen from (50) and (51) that in regions I–IV, $|\Delta P| \ll P$, similar to the DH case. However, in regions V and VI where excluded-volume effects are relatively small, $|\Delta P| \simeq P$ and there exist some points in the s/t diagram of states where $P = 0$. This fact shows that the electrostatic interaction can play a major role in the formation of different polyelectrolyte structures, such as polyelectrolyte complexes.[7]

VI. Conclusions

It has been shown that the RPA enables one to consider thermodynamic and screening properties of a weakly charged PES in the broad region of parameters which corresponds either to the overlapping of electrostatic blobs (at the moderate monomer concentrations) or to sufficiently high salt concentrations. Owing to the linear memory of monomers in a polymer chain the concentration dependencies of the screening radii and of the electrostatic contribution to the free energy turn out to be quite different from the DH ones.

The screening of the Coulomb potential of a test charge is oscillating in a poor solvents in contrast to the DH behavior. Moreover with the decrease of the solvent quality microphase separation into oppositely charged domains occurs, which is a first-order phase transition. The most probable (at least kinetically) structure formed after the microphase separation is a bcc lattice. When the salt concentration increases the microphase separation transforms into a usual macrophase one.

There are no thorough experimental investigations of a weakly charged polyelectrolyte solutions to our knowledge. A few experimental results mostly concern polyelectrolyte complexes.[6] The most direct experimental verification of our theory could be provided by means of the measurement of the correlation functions $G_{ij}(k)$, $G_q(k)$, or $G_\rho(k)$ (see eq 8, 38, and 39) by the methods of small-angle X-ray or neutron scattering. These functions should exhibit a strong correlation maximum. It should be noted that curves of similar type were observed also for ionomeric melts,[23] the maximum being attributed to ion clustering. We suppose that this phenomenon can be accounted for in the framework of our theory.

Appendix 1. Limits of the RPA Applicability

To determine the limits of the RPA applicability it is necessary to take into account the third term of expression 42. This term enables determination of the conditions, where higher order corrections owing to the $\Gamma_\rho^{(3)}$ vertex are irrelevant in comparison with the RPA one. Consider a weakly fluctuating basic polymer system ($\eta \ll 1$). Then $\Gamma_\rho^{(3)}$ can be obtained from eq 43 for an ideal polymer system. Surely in this case we can consider the RPA applicability only from the low monomer or salt concentration side. When these concentrations are sufficiently high, the RPA limits of applicability coincide with the DH ones:[12] $\rho r_s^3/m \gg 1$ and $c_i r_s^3 \gg 1$. The expansion parameter can be obtained by using the conventional diagrammatic technique.[23]

The monomer–monomer correlation function $G_\rho(k)$ is the propagator of the theory. Corrections to ΔF owing to
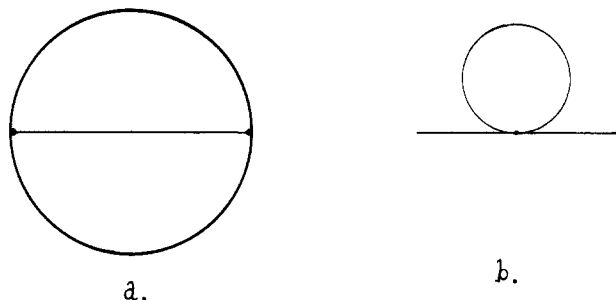

Figure 3. Higher order correction diagrams.

ΓF owing to $\Gamma_\rho^{(3)}$ are determined by the diagram of the type shown in Figure 3. This leads to

$$\int [\Gamma_\rho^{(3)}]^2 [G_\rho]^3 \, d^3 k_i \, d^3 k_2 \, d^3 k_3$$

which gives

$$\Delta F^{(3)} \simeq \frac{VT}{r_0^3} \left[\frac{\rho^*}{\rho} \right]^{3/4} \int \delta(\vec{x}_1 + \vec{x}_2 + \vec{x}_3) \times$$

$$(\vec{x}_1{}^2 + \vec{x}_2{}^2 + \vec{x}_3{}^2)^2 \prod_{i=1}^{3} \frac{d^3 x_i}{\vec{x}_i{}^2 + t + 1/(\vec{x}_i{}^2 + s)}$$

where ρ_* is the concentration corresponding to the overlapping of the electrostatic blobs and x_i are dimensionless wave vectors. Divergence of the integral at large x can be canceled by subtraction of the self-energy (in this case it is sufficient to restrict the limits of integration to $|\vec{x}| < 1$).

Comparison of $\Delta F^{(3)}$ with $\Delta F_{\rm RPA}$ under the condition of $s \simeq t \simeq 1$ gives the following expression for the perturbation theory parameter (PTP):

$$\mathrm{PTP} = \Delta F^{(3)}/\Delta F_{\rm RPA} = \left[\frac{\rho_*}{\rho} \right]^{3/4} = \left[\frac{r_0}{D} \right]^3$$

where D is the electrostatic blob size (see eq 1). For dilute solution at high salt concentration ($s \gg 1$)

$$\mathrm{PTP} = \frac{1}{s^{3/2}} \left[\frac{\rho_*}{\rho} \right]^{3/4} = \left[\frac{r_s}{D} \right]^3$$

Thus the RPA is valid from the low concentrations side when $\rho > \rho_*$ or when $r_s < D$.

When in a poor solvent ($t < 0$) we approach the spinodal at $s \leq 1$, where microphase separation should take place, the RPA will be also violated. Indeed to determine the PTP in this case we must use expressions 42 and 44. The change $\psi \to \lambda\psi$ in eq 44 does not alter the PTP, so the common multiplier $M = (1 - s)\rho a^2/r_0^2$ of the expansion can be transferred into ψ^3 or into ψ^4. Then the constant multiplier before the ψ^4 term will be $1/M$. The PTP can be determined as the two loop correction to the propagator[24] (more exactly to the "mass" $\Delta t/(1 - s)$ of expansion (44)). This correction is determined from the diagram shown in Figure 3b, and after certain transformations we get

$$\mathrm{PTP} =$$

$$\left[\int \frac{dx \, x_*^2/r_0^3}{\{\Delta t/[4(1 - s)] + (x - x_*)^2\} M} \right] \Big/ \left[\frac{t}{1 - s} \right] =$$

$$\frac{(1 - s)^{1/2}}{\Delta t^{3/2} \rho a^2 r_0}$$

So when PTP $\ll 1$ or $|\Delta t|^3 \gg (1 - s)/(\rho a^2 r_0)^2$ the RPA can be applied and it is violated only near the spinodal $\Delta t = 0$.

Appendix 2. Contribution of the Coulomb Interaction to the Free Energy at High Salt Concentrations

It is convenient in this case to choose for a characteristic polyelectrolyte parameter not r_0 (see eq 33) but r_{0f}:

$$r_{0f} = a \left[\frac{m^2}{u \rho a^3} \right]^{3/11} \left[\frac{B}{a^3} \right]^{1/11} \tag{2.1}$$

By use of eq 9, 32, and 32a and dimensionless variable $x = kr_{0f}$ it can be shown that

$$\kappa^2(x) = s_f + 1/x^{5/3} \tag{2.2}$$

where $s_f = r_{0f}^2/r_s^2$ and r_s is determined by eq 36. The Coulomb contribution to the free energy of PES, ΔF_c, can be obtained by substitution of eq 2.2 into (13):

$$\Delta F_c =$$
$$\frac{VT}{12\pi r_s^3} + \frac{VT}{4r_{0f}^3 s_f^{1/3}} \int_0^1 d\alpha \int_0^\infty \frac{dk\, k^2}{k^{11/3} + k^{5/3} + \alpha/s_f^{11/6}} \tag{2.3}$$

In this case the salt concentration is assumed to be high enough, it implies $s_f \gg 1$ and thus the integral (2.3) can be explained in powers of $1/s_f$. The integral (2.3) is not an analytic function of $\alpha/s_f^{11/6}$, and it can be estimated by means of dividing the limits of the integration:

$$\int_0^1 \frac{dk\, k^2}{k^{5/3} + \alpha/s_f^{11/6}} + \int_1^\infty \frac{dk\, k^2}{k^{11/3} + \alpha/s_f^{11/6}}$$

The asymptotic expansion of these integrals in $1/s_f$ then can be easily obtained:

$$\Delta F_c = -\frac{VT}{12\pi r_s^3} + \frac{VT}{r_{0f}^3 s_f^{1/3}} - \frac{VT}{r_{0f}^3 s_f^{9/5}} \tag{2.4}$$

The first term in eq 2.4 is the DH expression for the electrostatic energy of salt and of separate charges and the other two contributions come from the Coulomb interaction of monomers. Thus the total free energy of PES consists of the free energy of the basic polymer solution $F_0 \simeq VT/\xi^{3\,3}$] and of ΔF_c; ξ is the correlation radius (see eq 29 and 31).

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