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Microphase Separation in Weakly Charged Annealed Gels and Associating Polyelectrolyte Solutions

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ABSTRACT: Association-caused microphase separation in weakly charged polyelectrolytes dissolved in a good solvent is theoretically predicted. To this end, a theoretical treatment of the concentration fluctuations in solutions of homopolymer chains, containing small fractions of both charged groups and reversible stickers (groups A capable of association via thermoreversible reaction $A + A \leftrightarrows A_2$), is presented. Following Lifshitz, thermoreversible cross-linking is considered as an effective interaction leading to the appearance of an additional association-caused term in the expression for the free energy. The density–density correlation functions are calculated and the thermodynamic stability of the spatially homogeneous state toward both micro- and macrophase separation is analyzed within the random phase approximation (RPA). All possible spinodal curves are classified in the limiting case of the annealed gel (solution with fully associated reversible stickers). For partially associated stickers, the interplay of electrostatic and effective associative interactions is shown to lead, in certain ranges of parameter space, to the appearance of qualitatively new features of spinodal curves, such as LCST.

I. Introduction.

One of the most appealing features of a large class of polymer systems is their ability to form self-assembled highly ordered structures having a crystal symmetry. This phenomenon is traditionally referred to as the order–disorder transition (ODT) or supercrystallization (the prefix "super-" emphasizing that the periodicity lengths for the polymer systems under discussion are large compared with those of low-molecular crystals) and is due to the interplay of a short-range demixing tendency and a long-range stabilizing factor. As a result, with the increase of the short-range segregating factor, such systems undergo microphase separation instead of the more familiar macrophase demixing. More precisely, as shown in refs 1−3, a system undergoes ODT if its spatially homogeneous (uniform, disordered) state is getting unstable with respect to infinitesimal concentration fluctuations having a finite wavelength D_* and wavenumber $q_* = 2\pi/D_*$, the values of q_* and D_* being determined by the specific character of the stabilizing factor for the systems under consideration. In particular, this stabilizing factor may be due to connectivity of segregating monomer units as for block copolymers,[1−5] or the long-range Coulomb interaction of charged monomer units, as for polyelectrolytes,[6−10] or nonlocal character of entropy of mixing.[11]

The short-range segregating factor appearing in all the aforementioned systems is the same. Namely, it is described by the conventional Flory–Huggins term that is of the second order in concentrations and includes the conventional χ parameter(s).[12] Meanwhile, in many polymer systems there is another short-range segregating factor: association, or thermoreversible bonding, of certain "active" monomer units, a phenomenon attracting considerable attention in recent years.

A few theoretical works are devoted to the effects of such a thermoreversible association on thermodynami-

cal properties of the polymer systems with a special emphasis on their stability with respect to the coil–globule transition[13] or macrophase demixing.[14−23] All these works give basically identical predictions concerning the properties of the sol phase whereas description of the gel phase remains a matter of controversy. In particular, in refs 14−19 using so-called Flory approach the contribution to the total free energy due to association is supposed to have the same analytical form both below and above the sol–gel threshold, whereas in refs 20−23 different forms of the association free energy are presented, which are singular at the sol–gel threshold. Thermodynamics of aggregation also has been studied in several recent papers using both analytical methods[24,25] and computer simulations[26,27] However, to our knowledge, no work has been devoted so far to the analysis of the association effects in connection with possible microphase separation, which is, probably, related to the fact that only few theoretical works[21,28] have addressed the scattering properties of the self-associating (cross-linked) polymer systems (see also a review[16]).

It is this latter problem that we address in the present paper. We will show (to our knowledge, for the first time) that, due to thermoreversible association, in the weakly charged polyelectrolyte solutions microphase separation may occur at the good solvent conditions and will establish these conditions quantitatively. To this end, we consider here the scattering properties and the spinodal stability of the weakly charged thermoreversibly associating (cross-linking) polyelectrolyte solutions in the approximation equivalent to that of refs 14−19, i.e., assuming that no special singularity is characteristic of the sol–gel transition (The complications due to nontrivial structure of the infinite cluster of the associated chains outlined in refs 21−23 will be discussed elsewhere.) The paper is organized as follows. In section II, we derive the expression for the free energy of weakly charged associating polyelectrolyte solutions using the Lifshitz additivity approximation. In section III, we

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calculate the correlation functions of the aggregating system within the random phase approximation (RPA) and formulate conditions of the stability of these systems with respect to both macro- and microphase separation. In section IIIA, we analyze the results obtained in the limit of zero association. Unlike the previous works, in this section we explicitly allow for the temperature dependence of the electrostatic contribution to the free energy, which enables us to add some new interesting features to the earlier established basics of microphase separation in nonaggregating weakly charged polyelectrolyte solutions. In section IV, we consider in detail stability of fully (but reversibly) associated polymer solution (annealed gel) with respect to both macrophase separation and ODT we first predict in the annealed gels under the good solvent conditions. Using the properties of the annealed gels as an important reference system, in section V we consider the effects of partially and thermoreversibly aggregating groups. The general outline of the obtained results is given in section VI. A derivation of the contribution to the free energy due to the existence of cross-links is given in Appendix A.

II. The Lifshitz Approach and the Free Energy of Weakly Charged Associating Polyelectrolyte Solutions.

Let us consider a solution of homopolymer chains containing small fractions of charged groups and groups capable of forming thermoreversible cross-links. Because of the electroneutrality condition applied to the solution as a whole, some free counterions as well as, generally, some ions of added low-molecular salt are also present in the system. For simplicity, the counterions are assumed to be monovalent.

To write the free energy of the system as a functional of "smoothed" densities $\{\rho(\mathbf{r})\}$ in this work we will employ the Lifshitz approach[29,30] according to which the free energy functional can be represented as a sum of the structural term $\mathcal{F}_0$ and the interaction term $\mathcal{F}_*$:

$$F[\{\rho(\mathbf{r})\}] = \mathcal{F}_0[\{\rho(\mathbf{r})\}] + \mathcal{F}_*[\{\rho(\mathbf{r})\}] \quad (1)$$

Here $\mathcal{F}_0$ is the free energy of the "ideal" polymer system corresponding to the original one, i.e., that having the same distribution of the chemical bonds between the residues but no other interactions between them. This term accounts for a nontrivial entropic contribution due to connectivity of monomer units in chains and includes also entropy of ideal gas of the counterions and solvent molecules.

The effect of "all other interactions" is incorporated into the second term $\mathcal{F}_*$, which can be readily calculated under assumption that it does not depend on the distribution of the chemical bonds between the residues (i.e., molecular–structural distribution). Indeed, under this assumption $\mathcal{F}_*$ can be identified with the energetic contribution of separated monomer units to the free energy of the "system of broken units", i.e., a model low-molecular system, interactions between the particles of which are assumed to be identical to "all other interactions" actually existing between the monomer units of the original system.

It is worthwhile to stress that the free energy can be written as a sum of two uncoupled terms (the polymer conformational entropy and the energy of interactions in the "system of broken units") due to the existence of

two distinct scales in macromolecular systems: a macromolecular scale on which statistical averaging of polymer conformations takes place and a low-molecular one on which "smoothing" of interactions takes place. When both scales are comparable, the concept of the "quasi-monomers" introduced by Khokhlov[31] should be used. (The interrelation between the concept of quasi-monomers and the classic field-theoretical problem of removing the ultraviolet divergencies was discussed by Erukhimovich.[14])

In our case, taking into account the hard-core repulsion and van der Waals attraction of the residues, referred to as the volume interactions, electrostatic interaction between the charged monomer units and an additional effective attraction due to associating groups, one can write

$$\mathcal{F}_* = \mathcal{F}_{FH} + \mathcal{F}_{el} + \mathcal{F}_A \quad (2)$$

Consistent with the preceding remark, for our case eq 2 is valid for associating and volume interactions. For the long-range electrostatic interaction, the situation is generally somewhat more subtle. However, for the weakly charged polymer solutions considered in this paper, the main electrostatic input comes from interaction between sufficiently distant monomer units, so that $\mathcal{F}_{el}$ is already a functional of "smoothed" densities, which makes the additivity approximation in (2) valid for our case as well.

To account for the short-range interactions (i.e., hard-core repulsion and van der Waals attraction) we use the conventional Flory–Huggins lattice theory. Let v and $\rho(\mathbf{r})$ denote the volume of an elementary cell of the lattice and the number density of monomer units, respectively. Then $\phi(\mathbf{r}) = v\rho(\mathbf{r})$ is the polymer volume fraction and the Flory–Huggins contribution to the interaction free energy reads

$$\mathcal{F}_{FH} = \frac{T}{v}\int \, d\mathbf{r} \, \{(1 - \phi(\mathbf{r}))\ln(1 - \phi(\mathbf{r})) + \\ \chi\phi(\mathbf{r})(1 - \phi(\mathbf{r}))\} \quad (3)$$

where the first and second terms account for hard-core repulsion and van der Waals attraction, respectively; χ is the conventional Flory parameter. Contributions due to small compressibility as well as volume fractions of the counterions and salt ions have been neglected. Also, here and below the temperature is measured in energetic units (the Boltzmann constant is set to unity).

The electrostatic contribution to the free energy is

$$\mathcal{F}_{el} = \frac{1}{2}\frac{e^2}{\epsilon v^2}\int \, d\mathbf{r}_1 \, d\mathbf{r}_2 \frac{(f_c\phi(\mathbf{r}_1) - n(\mathbf{r}_1))(f_c\phi(\mathbf{r}_2) - n(\mathbf{r}_2))}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (4)$$

where e is the elementary charge; ϵ is the dielectric constant of the solvent, f_c is the fraction of charged monomer units, and the designation $n(\mathbf{r}) \equiv v\rho_c(\mathbf{r})$ has been introduced ($\rho_c(\mathbf{r})$ is the number density of counterions). Below we will refer to $n(\mathbf{r})$ as the counterion volume fraction.

The next important step is to find an adequate expression for the free energy input $\mathcal{F}_A$ due to presence of associating groups. In the Flory-like mean-field approximation, adopted in the present paper, it takes the following form:

$$\mathcal{F}_A = Tf_a \int \rho F_A(k\phi(\mathbf{r})f_a) \, d\mathbf{r} \quad (5)$$

Here f_a is the fraction of monomer units (stickers) capable of forming thermoreversible cross-links, $k = \tilde{k}/v$ is the dimensionless association constant (the parameter $\tilde{k}$ is defined in the Appendix by eq A3), and the function $F_A(y)$ may be written in terms of conversion (fraction of those stickers which actually did associate) p as follows:

$$F_A(y) = \frac{p}{2} + \ln(1 - p) \tag{6}$$

$$y = p/(1 - p)^2 \tag{7}$$

Dependence of conversion p on the association parameter $y = k\phi(\mathbf{r})f_a$ is determined by the mass action law 7. To our knowledge, first such an expression for F_A was presented in ref 13 and generalized in ref 14. Afterward it was repeatedly rederived and used in refs 17−19 and 21. One more derivation of this expression is given in the Appendix. (For the sake of simplicity we do not discuss in the present paper the more sophisticated approximation presented in ref 23.)

To calculate the entropic contribution $\mathcal{F}_0$ we use the random phase approximation (RPA) known to be quite satisfactory for the purposes of the present work. More precisely, we expand the "ideal" free energy functional $\mathcal{F}_0$ in the powers of fluctuations of volume fractions about their averaged (over the whole volume V of the system) values $\bar{\phi}$ and $\bar{n}$

$$\phi_1(\mathbf{r}) = \phi(\mathbf{r}) - \bar{\phi}, \; \phi_2(\mathbf{r}) = n(\mathbf{r}) - \bar{n} \tag{8}$$

$$\phi_i(\mathbf{q}) = \int d\mathbf{r} \; \phi_i(\mathbf{r}) \exp(i\mathbf{qr}) \tag{9}$$

and keep the first nonvanishing (quadratic in ϕ_i) terms:

$$\frac{\mathcal{F}_0}{T} = \frac{\mathcal{F}_0^{eq}}{T} + \frac{1}{2v} \int \frac{d\mathbf{q}}{(2\pi)^3} \Gamma_{ij}^0(\mathbf{q})\phi_i(\mathbf{q})\phi_j(-\mathbf{q}) \tag{10}$$

The matrix $\|\Gamma_{ij}^0(\mathbf{q})\|$ appearing in eq 10 is inverse to the structural matrix $\mathbf{g}(\mathbf{q})$, which describes effects of the polymer connectivity and is determined in the most general form for the flexible polydisperse multicomponent polymer systems as follows:[3,32,33]

$$g_{ij}(q) = \sum_S \nu_S \int d\mathbf{r}\langle\rho_i^S(\mathbf{r})\rho_j^S(0)\rangle_S \exp(i\mathbf{qr}) \tag{11}$$

$\rho_i^S(\mathbf{r})$ is the local density of all residues of the ith sort pertaining to a macromolecule characterized by structure S, ν_S is the average number of such macromolecules per unit volume and brackets $\langle\rangle_S$ imply averaging over all conformations of the macromolecule S (under assumption of Gaussian statistics).

For simplicity, we restrict ourselves in this paper to the case of monodisperse linear polymer chains characterized by the polymerization index N and Kuhn length a. Let ρ_1 and ρ_2 denote the number densities of the monomer units and counterions, respectively. Then for Gaussian chains and pointlike counterions the structure matrix $\mathbf{g}$ takes the form

$$vg_{11}(q) = \phi \, N f_D(x), \quad x \equiv \frac{q^2 a^2 N}{6}$$

$$g_{12} = g_{21} = 0, \quad vg_{22} = n_c = f_c\phi \tag{12}$$

where the last equality for the component g_{22} holds due

to the condition of overall electroneutrality of the salt-free solution and the component $g_{11}(q)$ for Gaussian chains is proportional to the Debye function (N is the degree of polymerization):

$$f_D(x) = 2\frac{e^{-x} - 1 + x}{x^2} \simeq \begin{cases} 1, & x \to 0 \\ \dfrac{2}{x}, & x \gg 1 \end{cases} \tag{13}$$

We will use these two asymptotic forms for the description of macrophase and microphase separations, thus always assuming that the chain size is much larger than the period of the emerging microstructure.

Collecting quadratic terms in the expansions in powers of ϕ_i of all three contributions appearing in the expressions for the total free energy (eq 2), we obtain the desired RPA expression for the free energy of associating polyelectrolytes:

$$\frac{\mathcal{F}}{T} = \frac{\mathcal{F}^{eq}}{T} + \frac{1}{2v} \int \frac{d\mathbf{q}}{(2\pi)^3} G^{-1}_{ij}(\mathbf{q})\phi_i(\mathbf{q})\phi_j(-\mathbf{q}) \tag{14}$$

Here $\mathcal{F}^{eq}$ denotes the free energy of the uniform state, which is in fact irrelevant for determination of the system scattering properties and stability, and components of the matrix $\mathbf{G}^{-1}$ are calculated as follows:

$$G^{-1}_{11}(q) = (vg_{11}(q))^{-1} + \frac{1}{1 - \phi} - 2\chi + \frac{4\pi u f_c^2}{(qa)^2} - \frac{2kf_a^2}{(1 + \sqrt{1 + 4kf_a\phi})\sqrt{1 + 4kf_a\phi}} \tag{15}$$

$$G^{-1}_{12}(q) = G^{-1}_{21}(q) = -\frac{4\pi u f_c}{(qa)^2} \tag{16}$$

$$G^{-1}_{22}(q) = \frac{1}{f_c\phi} + \frac{4\pi u}{(qa)^2} \tag{17}$$

Here, the reduced electrostatic parameter $u = (e^2 a^2)/(\epsilon T v) = (l_B/a)(a^3/v)$ (l_B is the usual Bjerrum length) has been introduced.

In the matrix $\mathbf{G}^{-1}(q)$, polymer entropy is described by the structure correlation function $g_{11}(q)$, which is q-dependent due to connectivity of the units in a chain. The entropy of ideal gas of counterions is the first term in $G^{-1}_{22}(q)$. The electrostatic interaction is accounted for in eqs 15−17 by the q-dependent (which reflects the long-range nature of electrostatics) terms proportional to the parameter u. The second and third terms in $G^{-1}_{11}(q)$ are due to hard-core repulsion and short-range van der Waals attraction and stem from the Flory−Huggins term $\mathcal{F}_{FH}$. The effect of associating groups (corresponding to $\mathcal{F}_A$) on the correlational properties of the solution is described by the last term in $G^{-1}_{11}(q)$.

III. Spinodals

To find the spinodal condition (under which the spatially homogeneous state of the solution becomes absolutely unstable with respect to infinitesimal density fluctuations) one should analyze in detail the matrix $\mathbf{G}^{-1}(q)$: obviously, the homogeneous state is stable if the matrix is positive definite. In this case, as can be seen from the general expression for the free energy (eq 14), density fluctuations lead to an increase of the free energy. Therefore, to find the spinodal, we should find

the condition when the matrix $\mathbf{G}^{-1}(q)$ ceases to be positive definite or, in other words, when the minimal eigenvalue of the matrix equals zero. However, in practical calculations it is more convenient to determine the spinodal by divergence of the polymer–polymer component of correlation function matrix $\mathbf{G}(q)$. It is readily obtained from eqs 15–17 by inverting the matrix $\mathbf{G}^{-1}(q)$:

$$[G_{11}(q)]^{-1} = (vg(q))^{-1} + \frac{1}{1-\phi} - 2\chi +$$
$$\frac{4\pi u f_c^2}{(qa)^2 + 4\pi u f_c \phi} - \frac{2k f_a^2}{(1+\sqrt{1+4kf_a\phi})\sqrt{1+4kf_a\phi}} \quad (18)$$

Comparing this expression for $(G_{11}(q))^{-1}$ with $(\mathbf{G}^{-1})_{11}(q)$ we notice that if counterions (as is our case) interact with other components of the system (solvent and polymer) only through electrostatic interactions their effect on the polymer–polymer correlations (thus stability of homogeneous state in our approximation) amounts to the usual Debye–Hückel screening of polymer charges.[8] This fact allows inclusion in the theory added low-molecular salt in the usual Debye–Hückel way. The corresponding effects will be investigated elsewhere, while in this work we consider only salt-free solutions.

Thus, we will find the spinodal by seeking a zero of $G_{11}(q)^{-1}$ given by (18), which corresponds to a divergence of polymer–polymer correlations. Another point is that since we are dealing with polyelectrolyte solutions, the possibility of both macro- and microphase separation should be considered, and therefore the critical wavevector, at which the homogeneous phase becomes unstable should be determined by seeking for a minimum in q of $G_{11}(q)^{-1}$. Summing up we can write the following set of equations determining the spinodal:

$$\begin{cases} [G_{11}(q)]^{-1} = 0 \\ \dfrac{d[G_{11}(q)]^{-1}}{dq}\Big|_{q=q_*} = 0, \ q_* \geq 0 \end{cases} \quad (19)$$

The character of phase separation is decided by the value of q_*: if the minimal value of $[G_{11}(q)]^{-1}$ is reached at $q_* = 0$, then the solution separates into macroscopic phases; if it is reached at $q_* > 0$, the separation goes on a microscopic scale, with $D_* = 2\pi/q_*$ giving the period of the emerging microdomain structure.

It is advantageous for subsequent analysis to rewrite the quantity $[G_{11}(q)]^{-1}$ in terms of conversion p related to the polymer volume fraction by eq 7:

$$[G_{11}(q)]^{-1} = (vg(q))^{-1} + \frac{1}{1-\phi} - 2\chi_{\text{eff}} +$$
$$\frac{4\pi u f_c^2}{(qa)^2 + 4\pi u f_c \phi} \quad (20)$$

$$\chi_{\text{eff}} = \chi + \Delta\chi_a, \ \Delta\chi_a = \frac{f_a p}{1+p}\frac{1}{2\phi} \quad (21)$$

It is clear from eqs 20 and 21 that cross-linking leads to the increase of the effective χ parameter and, therefore, acts as an effective attraction between the monomer units. This attraction becomes stronger upon the increase of both f_a and p. At constant values of f_a and p, the influence of cross-links increases for smaller ϕ, i.e., under dilution of the solution. However, it should be

stressed that $\Delta\chi_a$, unlike χ, depends on the polymer concentration (via concentration dependence of conversion p). On the other hand, because of the short-range character of the additional associative interaction (note that the cross-links are assumed to be pointlike in our consideration), $\Delta\chi_a$ does not depend on the wave vector q, just as is the case for the conventional Flory–Huggins χ parameter. Summarizing, the description of both dispersional and associative short-range attraction between monomeric units can be incorporated into a common effectively renormalized χ_{eff} parameter whose value depends on the polymer concentration.

We start analysis of the spinodals from briefly considering the effects of electrostatic interaction in nonassociating solutions. This system will be the reference one for investigating effects of charge in the original system.

A. Effects of Electrostatics. To investigate nonassociating solution we put $f_a = 0$ in eq 18, which "switches off" association effects. Thus, we arrive at the well-studied case of weakly charged polyelectrolyte solutions.[6,7,10] In this subsection we remind some basic results of these works; however, in contrast to these references we will explicitly allow for the change of the u parameter caused by the temperature change, which is a normal experimental situation (we do not discuss here another possibility: to vary χ via changing of solvent composition and, therefore, its quality). Since the electrostatic parameter $u = e^2 a^2/\epsilon T v$ also depends on the temperature, when calculating the spinodal u, it should be considered as a function of χ. In what follows we adopt the simplest model expression for the temperature dependence of χ

$$\chi = \frac{1}{2}\frac{\theta}{T} \quad (22)$$

where Θ is a value of the Flory Θ temperature. Thus, using the above-given definition of u we obtain

$$u = 2\chi u_\theta, \quad u_\theta \equiv \frac{e^2 a^2}{\epsilon\theta v} = \frac{l_\theta a^3}{a\,v} \quad (23)$$

where u_Θ and l_Θ are values of the electrostatic parameter and the Bjerrum length at the Θ temperature, respectively.

Supposing that the chains are sufficiently large to span many periods of microstructure so that the $x \gg 1$ asymptotics of the Debye function (13) is always valid, we arrive at the following spinodal equation:

$$\frac{(qa)^2}{12\phi} + \frac{1}{1-\phi} - 2\chi + \frac{4\pi u f_c^2}{(qa)^2 + 4\pi u f_c \phi} = 0 \quad (24)$$

Let us start the analysis by finding an expression for the period D and wavevector q_* characterizing critical fluctuations providing spinodal instability

$$(q_* a)^2 = (48\pi u(\chi_s)\phi f_c^2)^{1/2} - 4\pi u(\chi_s)\phi f_c, \ D_* = 2\pi/q_* \quad (25)$$

where $\chi_s(\phi, u, f_c)$ is the χ parameter corresponding to a spinodal point. The plots of the spinodal value of the microstructure period $D_* = 2\pi/q_*$ for different values of u_Θ and f_c are presented in Figure 1. It can be seen that D_*/a is numerically large, so that for weakly charged polyelectrolytes the period of microstructure lies in the
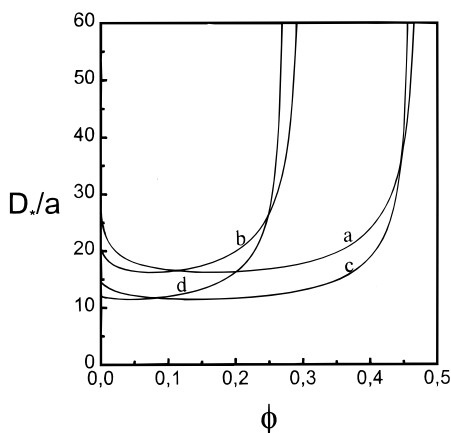
Figure 1. Dependence of the period of microstructure $D_*/a = 2\pi/(q_*a)$ on the polymer volume fraction ϕ for different values of electrostatic parameters: (a) $u_\Theta = 1$, $f_c = 0.05$; (b) $u_\Theta = 2$, $f_c = 0.05$; (c) $u_\Theta = 1$, $f_c = 0.1$; (d) $u_\Theta = 2$, $f_c = 0.1$.

region of tens of nanometers. Note that these period plots, calculated by varying the values of χ (hence u), differ qualitatively from those calculated in ref 10 for fixed values of u in two ways: (i) depending on the value of u_Θ and the concentration range, D_* may both decrease and increase upon the increase of the fraction of charged monomers f_c (were the χ dependence of u neglected, the increase of f_c would invariably result in the decrease in D_*); (ii) with infinite dilution the spinodal values of D_*/a shown in Figure 1 have finite limiting values

$$\frac{D_*^0}{a} = \frac{2\pi}{q_*^0 a}, \quad (q_*^0 a)^2 = 24\beta \frac{1-\alpha}{1+\alpha} \qquad (26)$$

$$\alpha \equiv \frac{\pi u_\Theta f_c}{3}, \quad \beta \equiv \frac{\alpha f_c}{1+\alpha} \qquad (27)$$

which depend on u_Θ and f_c, whereas the period considered in ref 10, at a fixed value of u (and χ), would become infinitely large in this limit. All curves exhibit a minimum, whose position is strongly dependent on the parameter u_Θ and weakly (via $u(\chi_{cr})$) on f_c. The initial decrease of D_* with increasing volume fraction is easily understood: the denser the charged system, the smaller the period must be. However, beyond a certain polymer volume fraction a further increase of concentration leads to the increase in D_*. As seen from eq 25, this is due to an increased screening of charges on the chains by free counterions. Indeed, the microdomain period scales with the concentration as $D_* \sim \phi^{-1/4}$ whereas the Debye–Hückel screening length due to counterions varies as $r_{DH} \sim \phi^{-1/2}$. Thus, the charges become increasingly screened with the increasing concentration, i.e., properties of the system increasingly approach those of the neutral one. Eventually, as follows from eq 25, q_*^2 vanishes at concentration

$$\phi_L = \frac{3}{\pi u} \qquad (28)$$

and formally becomes negative for $\phi > \phi_L$, which from a physical point of view means that the character of phase separation changes from micro- to macroscopic. The point $\phi = \phi_L$ is referred to as the Lifshitz point. Substituting (28) into (20) we get the following expressions for spinodal coordinates of the Lifshitz point:

$$\phi_L = 1 - \frac{1}{\dfrac{3}{\pi u_\Theta} + 1 - f_c} \qquad (29)$$

$$\chi_L = \frac{3}{\pi u_\Theta} \frac{1}{2\phi_L} \qquad (30)$$

We can see that for values of $u_\Theta \gg 1$ the Lifshitz point always exists at fairly large concentrations. Raising the value of u_Θ (at constant f_c), we observe from eqs 29 and 26 that for certain values of u_Θ the values of ϕ_L and ($q_*^0 a)^2$ may formally become negative, which is an indication that separation proceeds macroscopically for all concentration. Therefore, a physically meaningful ($0 < \phi_L < 1$) Lifshitz point exists only if the following condition is satisfied:

$$\alpha = \frac{\pi u_\Theta f_c}{3} < 1 \qquad (31)$$

Since in this work we consider only weakly charged polyelectrolytes, for them, as follows from their definition: $u_\Theta f_c^{1/2} \ll 1$ (see refs 34, 35, 6) inequality 31 holds always.

Substituting the critical wavevector (eq 25) into the spinodal eq 24 we reduce the system (eq 19) to the single equation containing only χ and ϕ

$$\frac{2(\pi u f_c^2)^{1/2}}{(3\phi)^{1/2}} - \frac{\pi u f_c}{3} + \frac{1}{1-\phi} - 2\chi = 0 \qquad (32)$$

where u is a function of χ given by (18). The spinodal curve $\chi(\phi)$ is easily obtained explicitly by solving this quadratic equation. Spinodal curves for different values of u_Θ and f_c are presented in Figure 2. In it the area below the spinodal line corresponds to stability of the homogeneous state, above this line—to phase separation (dashed and solid lines designate spinodals with respect to micro- and macrophase separation, respectively). The bold dashed curve is the spinodal for the reference neutral system (degree of polymerization $N = 1000$). It is seen that spinodals for neutral and charged systems do not differ qualitatively. Charging of the chains leads, as consistent with the results of refs 6, 7, and 10, to two effects: (i) it increases stability of the homogeneous state (all the spinodals for charged chains lie above the spinodal of the corresponding neutral system); (ii) it changes the character of the phase separation from macro- to microscopic (in a certain range of polymer volume fractions $\phi < \phi_L$ as discussed above). The increase of either u_Θ or f_c results in increased stability of the disordered state, so that the qualitative effect on the spinodal of variations of solvent polarity (u_Θ) and the fraction of charged monomers (f_c) is the same, since they both affect the strength of the electrostatic interaction. At the same time, we must bear in mind that the increase of u_Θ according to eq 29 considerably shifts the position of the Lifshitz point.

IV. Spinodals of Annealed Gels (Full Association).

Now we come to the main goal of the paper: determination of the stability of systems containing both charged and associating groups. To this end the full expression in (18) must be analyzed, taking into account the fact that the value of the association constant k
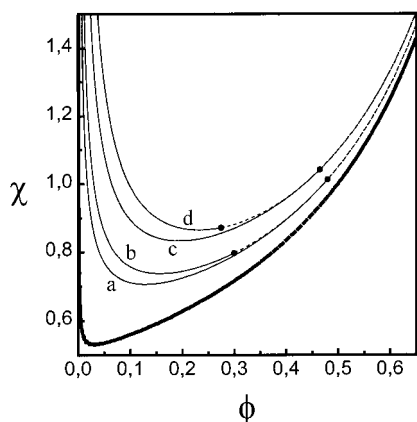
Figure 2. Spinodal curves of weakly charged polymer solutions for different values of electrostatic parameters (the notations are the same as in Figure 1). Solid lines indicate instability toward micro- and dashed toward macrophase separation. The Lifshitz points are shown by dots. The bold dashed curve is the spinodal for a reference neutral polymer solution (degree of polymerization $N = 1000$).

depends on temperature. In other words, the association constant k must be considered, like u, to be a function of χ. Thus, to obtain spinodal curves we need to know this function $k(\chi)$ which is parametrically given by functions $\chi(T)$ and $k(T)$ which should be specified explicitly. Generally, such a spinodal equation cannot be solved analytically and must, therefore, be treated numerically. Moreover, the results depend on the expression modeling the $\chi(T)$ dependence. Therefore, before proceeding to discussion of the results of our numerical calculations for an explicit dependence $k(\chi)$, in this section we analyze first the important limiting case of full association of stickers. This will further prepare the theoretical background for consideration of the realistic system with partial association conducted in the next section.

1. Completely Associated Neutral Polymer (Neutral Annealed Gel). First we consider the case when the polymer is electrostatically neutral ($f_c = 0$) and all stickers do, indeed, form the bonds ($p = 1$). The spinodal equation for this case is simply

$$\frac{1}{\phi N} + \frac{1}{1 - \phi} - 2\chi - \frac{f_a}{2\phi} = 0 \tag{33}$$

If f_a is larger than the critical value $2/N$, the corresponding system is, evidently, nothing but the annealed gel. Moreover, the inequality $f_a N \gg 1$ is typical for real experimental situations, in which case the first term in eq 33 as well as effects related to some small content of the sol-fraction can (and below will) be neglected. The spinodal curves for different values of f_a are presented in Figure 3 (the bold curve being the reference spinodal for the corresponding nonassociating system). We can see that the increase of the fraction of associating groups f_a leads to decreased stability of the homogeneous state (lowering of the curves). It must be stressed that since the association term in the correlation function (20) is q-independent, in the absence of charges only macroscopic phase separation is possible (thus, all the curves shown in Figure 3 are dashed).

A characteristic feature of all the spinodals is that they monotonically tend to $-\infty$ as the solution becomes infinitely diluted. Therefore, for any polymer volume fraction the phase separation (for sufficiently large
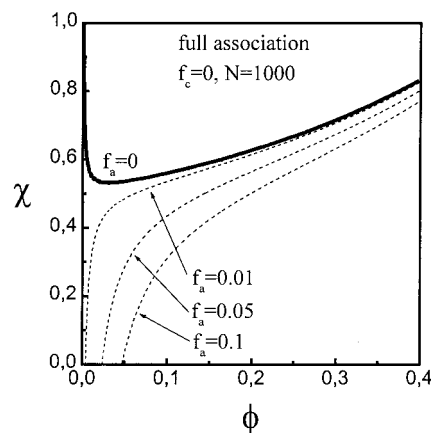
Figure 3. Spinodal curves of a completely associated neutral polymer solution (annealed gel) for different values of the fraction of stickers f_a. The bold curve is a reference spinodal for neutral polymer solution without cross-links ($N = 1000$). Since the system is electrostatically neutral, phase separation proceeds only macroscopically (indicated by dashed lines).

values of χ) proceeds into a pure solvent and polymer-rich phase. Such a peculiar type of phase separation is known to be a distinctive feature of gels and called syneresis. Obviously, because of this syneresis feature of this class of spinodals, for

$$\phi < \phi_\Theta = 2/(1 + \sqrt{1 + 8/f_a}) \tag{34}$$

the macrophase separation occurs in good solvent (i.e., for $\chi < 1/2$). Moreover for

$$\phi < \phi_0 = f_a/(2 + f_a) \tag{35}$$

χ formally becomes negative. Physically this means that for such small ϕ the system is unstable with respect to syneresis for any meaningful value of χ. The interplay of cross-linking attraction and hard-core repulsion is also characterized by the fact that the spinodal in (33) has an inflection point with the following coordinates:

$$\phi_i = \frac{(f_a/2)^{1/3}}{1 + (f_a/2)^{1/3}}, \quad 2\chi_i = (1 + (f_a/2)^{1/3})(1 - (f_a/2)^{2/3}) \tag{36}$$
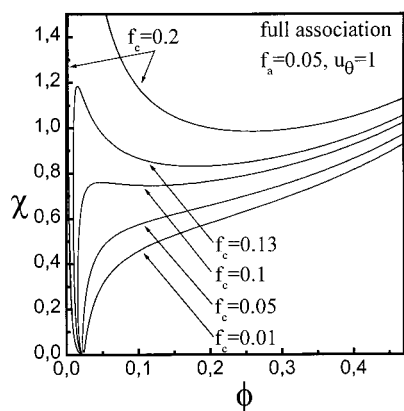
Note that ϕ_Θ, ϕ_0, and ϕ_i monotonically increase with increasing f_a, whereas the function $\chi_i(f_a)$ has a maximum at $f_a^m \approx 0.07$, with the maximum value $\chi_i(f_a^m) \approx 0.59$.

2. Completely Associated Weakly Charged Polymer (Annealed Charged Gel). Next we consider the weakly charged fully associated polymer (annealed charged gel). The spinodal equation in this case reads

$$\frac{2(\pi u f_c^2)^{1/2}}{(3\phi)^{1/2}} - \frac{\pi u f_c}{3} + \frac{1}{1 - \phi} - 2\chi - \frac{f_a}{2\phi} = 0 \tag{37}$$

where the term $1/(N\phi)$ is neglected as explained in the previous subsection. Taking into account the $u(\chi)$ dependence given by eq 23, one can find the following explicit expression for the spinodal curve:

$$2\chi_\pm = \left(\frac{\sqrt{\dfrac{\alpha f_c}{\phi}} \pm \sqrt{\dfrac{\alpha f_c}{\phi} - (1 + \alpha)\left(\dfrac{f_a}{2\phi} - \dfrac{1}{1 - \phi}\right)}}{1 + \alpha} \right) \tag{38}$$

Figure 4. Spinodal curves of a completely associated polyelectrolyte solution (annealed charged gel) for different values of the fraction of charged monomers f_c. Solid lines indicate instability with respect to microphase separation. For $f_c = 0.2$ the spinodal consists of two infinitely growing curves.
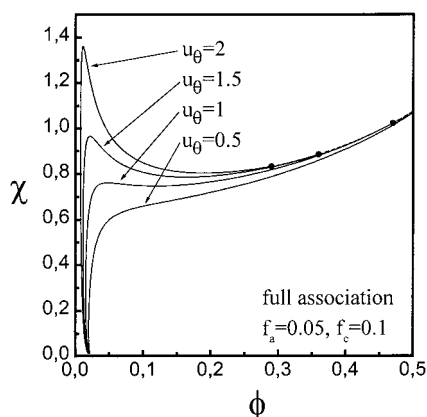
Figure 5. Spinodal curves of a completely associated polyelectrolyte solution (annealed charged gel) for different values of u_θ. Solid lines indicate instability toward micro- and dashed toward macrophase separation. The Lifshitz points are shown by dots.

Figure 4 presents the spinodal curves for different values of f_c at a fixed value of f_a and u_Θ, thus demonstrating the effect of charging the gel, while in Figure 5, the varied property is u_Θ (change in the dielectric constant of the solution), and f_c and f_a remain fixed. We see that for $\phi < \phi_m$ the syneresis remains a feature of the system since the polymer remains gelated. But now, because of the presence of charges on polymer chains, the separation may proceed either micro- (dashed curves) or macroscopically (solid curves). Note that both f_a and f_c influence the period of microstructure D_* and the Lifshitz point position since u depends on χ. Obviously, a change in u_Θ also leads to a shift of the Lifshitz point as shown in Figure 5. As would be expected from the stabilizing effect of the electrostatic interaction, the increase of u_Θ or/and f_c results in the considerable increase of the stability of the system, especially in the region of small concentrations. Beside that further increase of either u_Θ or f_c leads to the emergence of a peak in the spinodal curve.

The spinodal curves have two branches corresponding to two different signs in eq 38. The lower branch exists only for small values of ϕ satisfying the inequality 35. (Indeed, for $\phi > \phi_0$ this branch corresponds to unphysical negative value of χ and, therefore, it should be disregarded.) If the annealed gel is relatively strongly charged so that the inequality

$$\beta \equiv \frac{\alpha f_c}{1 + \alpha} > \frac{f_a}{2} \qquad (39)$$

holds, then both upper and lower branches of the spinodal infinitely grow in the limit $\phi \to 0$ (for values of u_Θ and f_a specified in Figure 4, this condition is calculated to be $f_c > 0.17$). However, for weakly charged polyelectrolytes such situation takes place only for rather small values of f_a. If the annealed gel is not strongly charged (inequality opposite to (39) holds), then the two branches exist only in the interval

$$\phi_0 > \phi > \phi_r = \frac{f_a - 2\beta}{2 + f_a - 2\beta} \qquad (40)$$

Thus, if the polymer volume fraction ϕ is fixed in the narrow interval (ϕ_r, ϕ_0), then the change of system state with the temperature is reentrant: the system is stable at intermediate temperatures ($\chi_+(\phi) > \chi > \chi_-(\phi)$) and unstable outside this interval, i.e., if the temperatures are high or low enough. The value of χ and the period D_* in the return point where the two branches merge are

$$2\chi_r = \frac{1}{\phi_r} \frac{\beta}{1 + \alpha} \qquad (41)$$

$$\frac{D_*^r}{a} = \frac{2\pi}{q_*^r a}, \quad (q_*^r a)^2 = \frac{12\beta}{1 + \alpha} \qquad (42)$$

It is interesting to see, comparing eqs 26 and 42, that the microstructure period emerging in the return point equals $\sqrt{2}$ times the period of the pure polyelectrolyte in the limit of zero polymer concentration.

Therewith, if the values of the electrostatic parameters β and $f_a/2$ do not differ much, then the upper spinodal branch has a pronounced peak (see Figure 4, curve for $f_c = 0.13$). The less the value of the ratio $2\beta/f_a$, the smaller the difference between the spinodals for charged and neutral annealed gels; the charged gels staying a bit more stable with respect to syneresis.

As can be seen from Figures 4–6 due to the interplay of counteracting associative and electrostatic interactions there exists a region of parameter space where the spinodal curves exhibit a broad plateau; χ_s value is rather insensitive to variation of ϕ in a rather broad range of concentrations. We find these values of solution properties as functions of (ϕ, χ) by demanding that the following conditions be satisfied:

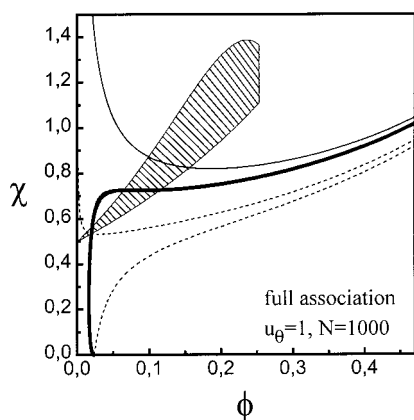$$\frac{\partial \chi(\phi)}{\partial \phi} = 0 \qquad (43)$$

$$\frac{\partial 2\chi(\phi)}{\partial \phi^2} = 0 \qquad (44)$$

This set of simultaneous equations can be solved explicitly:

$$f_a = 6z^2 + 8z^3, \ z \equiv \frac{\phi}{1 - \phi} \qquad (45)$$

$$f_c = \frac{16z^3(1 + z)^3}{1 - 2\chi + 6z + 9z^2 + 4z^3} \qquad (46)$$

Figure 6. Bold curve: an example of a spinodal with a plateau ($f_a = 0.05$, $f_c = 0.094$, $u_\Theta = 1$, $N = 1000$). Other curves are spinodals for all the reference systems: (a) neutral, nonassociating; (b) neutral, fully associated; (c) charged, nonassociating; (d) charged, fully associated. Solid lines indicate instability toward micro- and dashed toward macrophase separation. Hatched area corresponds to the region of parameter space (χ, ϕ) where the inflection point can be situated.

$$\frac{\pi u_\Theta}{3} = \frac{16 z^3 (1 + z)^3}{2 \chi f_c^2} \qquad (47)$$

An example of the curve with the plateau is presented in Figure 6 where we also illustrate the interplay of charges and cross-links leading to its appearance by plotting the spinodal curves for all the reference systems: (i) neutral, nonassociating; (ii) charged, nonassociating; (iii) noncharged, fully associated; (iv) charged, fully associated. Note that solutions of (45)−(47) are physically meaningful only if the parameters satisfy the following conditions:

$$f_a < 1, \quad f_c < 1, \quad u_\Theta f_c^{1/2} < 1 \qquad (48)$$

The last one is the validity condition for the approximation of weakly charged polyelectrolytes. In Figure 6, the region of (ϕ, χ) where the conditions in (48) are satisfied is hatched.

V. Spinodals of Partially Associated Polyelectrolyte Solutions

Now we finally consider stability of realistic systems containing both charged and partially associated groups. Therewith, for definiteness, we adopt T dependence of (22) for χ and the approximation for k, given in the Appendix (eq A3), which leads to the following function $k(\chi)$

$$k = k_0 e^{-\epsilon \chi}, \quad \epsilon \equiv \frac{2E}{\Theta}, \quad k_0 \equiv \frac{\tilde{k}_0}{v} \qquad (49)$$

where E is the energy of bond formation (which is, naturally, expected to be negative) and $\tilde{k}_0$ is a preexponential factor connected with the cross-link volume.

To calculate the spinodal curves $\chi(\phi)$, both dependences $k(\chi)$ and $u(\chi)$ must be substituted into eq 18 and the resulting system of simultaneous equations (eq 19) solved numerically. If this solution results in a finite value of q_* the spinodal equation can be reduced, similarly to eq 32 for nonassociating polyelectrolytes, to the form

$$\frac{2(\pi u f_c^2)^{1/2}}{(3\phi)^{1/2}} - \frac{\pi u f_c}{3} + \frac{1}{1 - \phi} - 2\chi - \frac{p(y)}{1 + p(y)} \frac{f_a}{\phi} = 0 \quad (50)$$

where $y = k \phi f_a$ and $p(y)$ is determined by the mass action law (7).

For uncharged partially associated polymers $f_c = 0$ and this spinodal equation takes the form

$$\frac{1}{\phi N} + \frac{1}{1 - \phi} - 2\chi - \frac{p(y)}{1 + p(y)} \frac{f_a}{\phi} = 0 \qquad (51)$$

where we again, as in eq 33, included the term $(\phi N)^{-1}$ negligible for charged polymers with a finite value of f_c. As discussed in the Introduction, section II and the Appendix, the latter equation is identical to that which would follow within the Flory approach adopted and developed in refs 14−19. Therefore, we will not discuss here the phase behavior of uncharged partially associated polymers and proceed at once to the case of charged ones.

It follows from the expression for k (eq 49) that two parameters (ϵ and k_0) should be specified to model a dependence $k(\chi)$. In principle, it could be done by the straightforward quantum-mechanical calculation of the association constant for the reversible bonding of the corresponding functional groups. We plan to return to this problem elsewhere in more detail, but in this paper we restrict ourselves by giving a general overview of the associating polyelectrolyte solutions behavior for different choices of the parameters ϵ and k_0. The typical spinodal curves are presented in Figures 7−9.

The bold curves are the spinodals of the two reference systems: the upper bold curve corresponds to the charged nonassociating system, the lower bold spinodal− to the charged annealed gel. These two limiting cases delineate the range within which the real spinodal curves (for partial association) lie. Let us preliminarily note that since now the degree of association depends on the thermodynamic state of the system, the spinodal curves of Figures 7−9 differ qualitatively from those of annealed gels (Figures 3−5) in that now the solution always becomes stable under sufficient dilution so that the spinodal curve infinitely increases as the solution becomes infinitely diluted.

Figure 7 illustrates the dependence of the stability on the value of the reduced energy of bonding ϵ when the preexponential factor k_0 is not large. We see that in this case the increase in the absolute value of ϵ leads to a continuous change from the nonassociating limiting curve to the fully associating one. Therewith, instead of syneresis in a strict sense (instability with respect to phase separation into a pure solvent and polymer-containing phase) the chosen partially cross-linked solution reveals a minimum of stability, this minimum becoming deeper for larger values of $|\epsilon|$.

Figure 8 illustrates the dependence of the stability on the value of the prefactor k_0 in a situation when the defined by eq 49 reduced energy of bonding ϵ is small so that the association constant k only weakly depends on the temperature (and thus χ). As we can see, if values of the prefactor k_0 are not large enough (curve a), then the effect of association results only in a small shift of the spinodal values of χ down (the temperature up) as compared with those for the corresponding polyelectrolyte solution without any association. For larger values of k_0 the effects of association are getting more and more pronounced. For $k_0 > f_a^{-2}$ there appear regions of
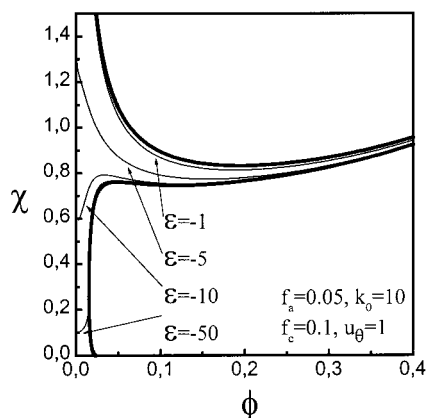
Figure 7. Spinodal curves of a partially associated polyelectrolyte solution for different values of ϵ and constant $k_0 = 10$. Phase separation proceeds microscopically (solid lines). The upper and lower solid curves are the spinodals for reference nonassociating and fully associated charged solutions, respectively.
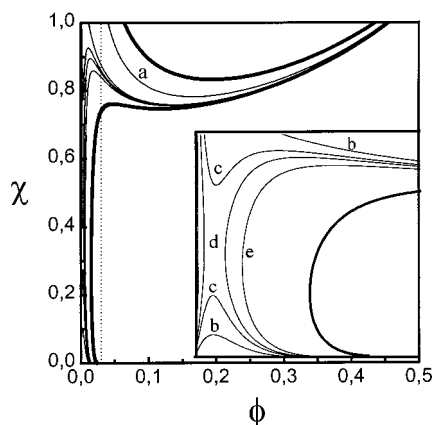
Figure 8. Spinodal curves of a partially associated polyelectrolyte solution for different values of k_0: (a) 100; (b) 1500; (c) 2000; (d) 2300; (e) 3000. The parameters for all the curves: $f_c = 0.1$, $u = 1$, $f_a = 0.05$, and $\epsilon = -1$. Phase separation proceeds microscopically (solid lines). The upper and lower solid curves are the spinodals for reference nonassociating and fully associated charged solutions, respectively.
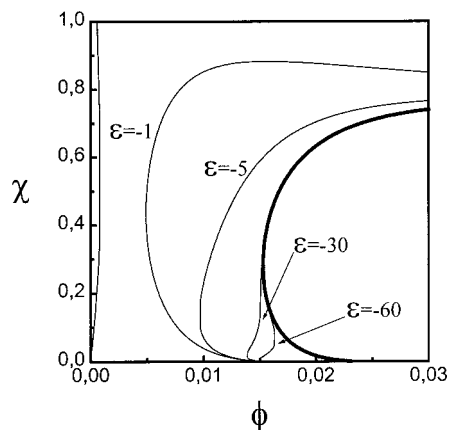
Figure 9. Spinodal curves of a partially associated polyelectrolyte solution for different values of ϵ, and constant $k_0 = 2500$. Other parameters are as in Figure 8. The scale of this plot corresponds to that of the inset of Figure 8. The bold line is a spinodal for a reference fully associated charged polymer solution.

thermodynamic instability at small values of χ (curves b and c) corresponding to the emergence of a lower critical solubility temperature (LCST); under the further

increase of k_0 a local maximum appears (curve c) analogous to the peak characteristic of the annealed charged gels considered above. This peculiarity is easily explained as follows: for small values of χ the electrostatic interaction parameter u is small, so that electrostatic interactions are weak. On the other hand, in approximation 49, the associative attraction stays finite even in the limit $\chi = 0$. Hence, the effect of destabilizing the homogeneous state due to association can be stronger for small values of χ (high temperature) than the stabilizing influence of charges which causes the appearance of the region of instability at small χ. For still larger values of k_0, the two regions of instability join and a region of concentrations (corridor of instability) appears (curves d and e) where the homogeneous state of the solution is unstable for any temperature. This corridor broadens with the further increase of k_0 and is, actually, a reminiscence of the syneresis existing in annealed charged gels. Thus, similar to the latter case, the reentrant spinodal in a narrow interval of concentration may be observed for partially associating polyelectrolytes as well.

Finally, Figure 9 illustrates some fine details of the spinodals in the low concentration region for different values of the reduced energy of bonding ϵ when the preexponential factor k_0 is large enough. We see that in this case the increase in the absolute value of ϵ leads not only to a broadening of the corridor of instability, but also to a qualitatively new feature: S-shape form of the spinodal, i.e., *multiple* re-entrant instability.

VI. Conclusion.

Summarizing, the main results we obtained in the present paper are as follows. For the case of almost complete association (annealed gel limit) the types of this behavior are determined primarily by the relationship between the fraction of associating groups (stickers) f_a and the specific electrostatic parameter β defined in (27).

If the reduced fraction of stickers $\zeta = f_a/\beta$ is small, then the phase stability of the system is close to that of nonassociating polyelectrolytes and the presence of cross-links is equivalent only to a small additional deterioration of the solvent. This correction can be neglected since destroying of the homogeneous state of these systems takes place already in bad solvent conditions. In the good solvent the presence of the minor (under the condition $\zeta \ll 1$) amount of cross-links practically does not influence the fast decay of the correlations (that at certain conditions could oscillate[6]) peculiar for the weakly charged polyelectrolyte solutions, and, therefore, stability of the latter.

On the contrary, for large reduced fraction of stickers ($\zeta \gg 1$), the spinodal of the system is close to that of noncharged annealed gels whose syneresis can proceed under the good solvent conditions. However, the fact of charging the chains changes drastically the morphology of the concentrated gel phase: instead of being spatially homogeneous, it becomes an ordered phase having a crystal symmetry, the period of the corresponding lattice being defined by eq 25. The physical meaning of the ratio $\zeta = f_a/\beta$ may be readily understood from the definition in (42) and the concomitant discussion: it is nothing but the squared ratio of the microstructure period D_* to the average spatial distance between stickers $af_a^{-1/2}$. Putting it in other words, if stickers are separated by a distance larger than D_*, they do not

influence much both the spinodal period and temperature of a polyelectrolyte solution; in the opposite limit the spinodal period D_* also does not change much, but the spinodal temperature dropped drastically. Putting it in other words, if $\zeta \gg 1$, then in a rather broad region of low and moderate polymer concentrations the system is expected to undergo microphase separation in good solvent conditions.

At last, at the crossover $f_a \sim \beta$, the interplay of the electrostatic and association effects leads to peculiar plateau spinodals described in section IV.

In the region of relatively small polymer densities where the association of the stickers is only weak or still stays far from being complete, more subtle effects such as an LCST type behavior and re-entrant (or even repeatedly re-entrant) phase transitions can take place. The shape of spinodal (and binodal) curves in this region is rather susceptible to the character of an actual temperature dependence of the association constant and requires additional analysis.

It is worthwhile also to stress that in the present work we restricted ourselves by finding the principle character (micro or macro) of phase separation and the corresponding spinodal conditions to which end it was sufficient to keep in the free energy expansion (eq 14) only terms up to the second order in ϕ_i. To obtain a full phase diagram (binodals and coexistence lines) and determine the specific symmetry of the ordered phases, one should take into account terms of the higher order in ϕ_i omitted for simplicity in (14). The corresponding calculations could be done quite similarly to those performed for weakly charged nonassociating polyelectrolyte systems both via weak and strong segregation approach in refs 9, 10, and 37 and refs 38 and 39, respectively. The only modification to the present case of associating polyelectrolytes would be the inclusion of additional terms in the vertexes arising from the association-caused free energy term F_A. Thus, by analogy with refs 9, 10, and 37–39 one can expect arising of a region corresponding to an ordered phase (most probably a lamellar or hexagonal one) at intermediate polymer concentrations and demixing of the solution into such an ordered phase and a disordered polymer-rich or solvent-rich phase at higher and lower polymer concentrations, respectively. We propose to carry out a proper quantitative analysis elsewhere.

Thus, we demonstrated in the present paper via a straightforward RPA calculation of the correlation functions and spinodals of the weakly charged thermoreversibly associating polyelectrolyte solutions that they reveal a rather rich phase behavior whose most spectacular feature is possibility to undergo, due to thermoreversible association, microphase separation under the good solvent conditions. New experiments in this field (primarily using scattering techniques) are necessary to check these predictions.

Appendix A: The Association-Caused Contribution F_A to the Free Energy.

In this Appendix we present a modified derivation of the association-caused contribution F_A to the total free energy which was first found by Lifshitz et al.[13] Let us consider a low-molecular system of monomer units A capable of associating into dimers A_2 via forming a thermoreversible chemical bond. We neglect all interactions between the monomer units and dimers except the association via the reversible chemical reaction

$$A + A \leftrightarrows A_2 \qquad (A1)$$

characterized by an association constant $\tilde{k}$. Then in accordance with the Mayer theory of nonideal gases, the thermodynamic behavior of the system under consideration is described by the generating function of all connected diagrams $\chi(z)$, which in our case consists only of two terms representing the contributions of monomer units and dimers, respectively:

$$\chi(z) = z + \frac{\tilde{k}z^2}{2} \qquad (A2)$$

Here $z = \Lambda^{-3}\exp(\mu/T)$ is the fugacity of the groups A (μ and Λ are the chemical potential of monomer units and the thermal de Broglie wavelength, respectively). For the sake of simplicity we assume that the temperature dependence of $\tilde{k}$ is given by

$$\tilde{k} = \tilde{k}_0 \exp(-E/T) \qquad (A3)$$

where E is the energy of the bond A–A and the temperature dependence of the prefactor $\tilde{k}_0$ (having dimensionality of volume) here is supposed to be weak enough to be neglected. To obtain an explicit expression for the free energy of the thermodynamically equilibrium reacting mixture, we use the following well-known relations which can be considered as a parametric definition of the pressure P as a function of the overall concentration ρ_a of the associating monomer units:

$$P/T = \chi(z) = z + \frac{\tilde{k}z^2}{2} \qquad (A4)$$

$$\rho_a = z\frac{\partial \chi(z)}{\partial z} = z + \tilde{k}z^2 \qquad (A5)$$

The explicit expressions for the chemical potential μ and fugacity z as functions of ρ_a follow from eq A5:

$$\frac{\mu}{T} = \ln(z\Lambda^3) \qquad (A6)$$

$$z = \frac{2\rho_a}{1 + \sqrt{1 + 4\tilde{k}\rho_a}} \qquad (A7)$$

Now, using eqs A4, A6, and A7 and the fundamental thermodynamic relation

$$\frac{F(N_a,V)}{V} = \rho_a\mu(\rho_a) - P(\rho_a) \qquad (A8)$$

we arrive at the following expression for the density of the free energy as an explicit function of ρ_a:

$$\frac{F}{TV} = \rho_a\ln\left(\frac{\rho_a\Lambda^3}{e}\right) - \rho_a\ln\frac{1 + \sqrt{1 + 4\tilde{k}\rho_a}}{2} + \frac{2\tilde{k}\rho_a^2}{(1 + \sqrt{1 + 4\tilde{k}\rho_a})^2} \qquad (A9)$$

On the other hand, the free energy can be represented, consistent with the Lifshitz approach, as the sum

$$\frac{\mathscr{F}}{TV} = F_{id}(\rho_a) + F_A(\rho_a) \tag{A10}$$

The first term in the rhs of eq A10 is the specific free energy of the ideal system of noninteracting monomer units (which in our case means nonassociating units)

$$F_{id}(\rho_a) = \rho_a \ln\left(\frac{\rho_a \Lambda^3}{e}\right) \tag{A11}$$

and it is nothing but the first term in the rhs of eq A9. Therefore, the desired specific association-caused contribution to the total free energy density $F_A(\rho_a)$ is given by the two last terms of eq A9:

$$F_A(\rho_a) = \frac{2\tilde{k}\rho_a^2}{(1 + \sqrt{1 + 4\tilde{k}\rho_a})^2} - \rho_a \ln\frac{1 + \sqrt{1 + 4\tilde{k}\rho_a}}{2} \tag{A12}$$

It will be useful in the following to present the results in terms of the experimentally observable fraction p (called conversion) of the groups associated into dimers rather than those of the association constant $\tilde{k}$. To this end we note that according to the general Mayer formalism the concentrations ρ_1 and ρ_{a2} of monomer units and dimers, respectively, are given by

$$\rho_1 = z, \quad \rho_2 = \tilde{k}\frac{\partial z}{\partial \tilde{k}} = \frac{\tilde{k}z^2}{2} \tag{A13}$$

On the other hand, it follows from the definition of p, that $2\rho_2 = p\rho_a$. Using expression A7 for the fugacity z as a function of ρ_a, we arrive at

$$p = \frac{4\tilde{k}\rho_a}{(1 + \sqrt{1 + 4\tilde{k}\rho_a})^2} \tag{A14}$$

As we can see, conversion p depends only on one association parameter $\tilde{k}\rho_a$, this product describing the balance of the entropic loss and energetic gain connected with a formation of a cross-link. In the main text, we use a dimensionless expression for p, which is a function of $\tilde{k}\rho_a = k\phi_a$.

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