# Weak crystallization and structural phase transitions in weakly charged polyelectrolyte systems

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Structural phase transitions of the weak crystallization type and an equilibrium between the corresponding phases in weakly charged polyelectrolyte systems are considered. A general method is proposed for the construction of the relevant Hamiltonian. It is reduced to the Landau–Brazovskiĭ Hamiltonian for the specific case of a melt of weakly charged and uncharged polymers. An alternative formulation of the Brazovskiĭ approximation is based on the variational principle, which is convenient for the calculation of the correlation functions and of the free energy of the systems described by this Hamiltonian; it is assumed that the radius of the first coordination sphere of the coexisting lattices and the unrenormalized (bare) vertices of the Hamiltonian describing them are different. These results are used in numerical calculation and analysis of the investigated system both in the mean-field and Brazovskiĭ approximations. It is shown that supercrystalline phases may appear and they may coexist with one another and with liquid phases. The conditions are identified for selecting real systems in order to observe the phase diagram under discussion and also of other Coulomb systems which can have similar phase diagrams.

## 1. INTRODUCTION

Systems which may exhibit a structural phase transition due to an absolute instability against fluctuations of the components of the order parameter with a finite wavelength $L$ and a corresponding wave number $q_0 = 2\pi/L$ are currently attracting attention. An analysis of phase transitions due to such an instability is the task for what is known as a theory of weak crystallization[1-4] which deals with the behavior of systems which for a scalar order parameter are described by the Hamiltonian

$$H(\{\varphi(\mathbf{q})\},T)=\frac{1}{2!}\int[\tau+(q-q_0)^2]\varphi(\mathbf{q})\varphi(-\mathbf{q})\frac{d\mathbf{q}}{(2\pi)^3}$$
$$+\frac{1}{3!}\int\gamma(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3)\prod_{i=1}^{3}\varphi(\mathbf{q}_i)\frac{d\mathbf{q}_i}{(2\pi)^3}$$
$$+\frac{1}{4!}\int\lambda(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)\delta(\mathbf{q}_1+\mathbf{q}_2+\mathbf{q}_3+\mathbf{q}_4)\prod_{i=1}^{4}\varphi(\mathbf{q}_i)\frac{d\mathbf{q}_i}{(2\pi)^3},$$

where $\varphi(\mathbf{q}) = \int dV\Phi(\mathbf{r})\exp(i\mathbf{qr})$ is the Fourier transform of the order parameter $\Phi(\mathbf{r})$ (here and below the functions in the coordinate representation will be represented by capitals and their Fourier transforms by the corresponding lower-case letters); $\tau$ is the effective temperature; a characteristic momentum $q_0$ and the vertex functions $\gamma$ and $\lambda$ are usually assumed implicitly to be the same for all the phases, i.e., they can be regarded as special chemical potentials (or their combinations).1)

Although the best known applications of this theory are to liquid crystals, systems which are relatively low-molecular,[3-5] it has also been used successfully in discussing structural phase transitions due to instabilities in multicomponent polymer systems.[6-12] The order parameter is in this case the vector representing the concentrations of polymer links of various kinds and the corresponding transitions in the physics of polymers are usually called microphase stratification, formation of a domain structure, or supercrystallization; it should be noted that the term supercrystallization is used in the case of a large parameter $L/a$, where $a$ is a characteristic microscopic scale of the system. The special features of the application of the theory of weak crystallization to polymer systems are: 1) it is possible to obtain expressions for the leading vertices of the effective Hamiltonian explicitly by microscopic analysis; 2) there are additional features because in the case of some polymer systems the parameter $q_0$ and the functions $\gamma$ and $\lambda$ may be state functions that differ for the coexisting phases. It would be of special interest for the development and application of the theory of weak crystallization to analyze the singularities in the specific case of a phase equilibrium in concentrated systems of charged macromolecules whose behavior is quite universal. Such an analysis is given below.

The features of the behavior of systems of charged particles due to their long-range Coulomb interaction have always attracted the attention of physicists (see for example, Ref. 13). Charged polymer systems are particularly interesting because of their special nature, which is responsible for the much greater range of behavior than that of low-molecular electrolytes and is due to the general properties specific to high-polymer systems; such systems have an anomalously low (compared with low-molecular systems) configurational entropy, a high susceptibility to external perturbations, and a large correlation radius. In particular, as demonstrated first in Refs. 8–11 (see also Refs. 14 and 15), a specific (compared with low-molecular electrolytes) behavior is exhibited by a number polyelectrolyte systems under conditions for which in the case of an uncharged polymer one would expect stratification into two phases with different concentrations of the polymer, such that the improvement of the energy of the short-range interaction between the links

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would have exceeded the loss of the entropy resulting from the nonuniform spatial distribution of macromolecules. In fact, in the case of charged polymers this stratification is much less favorable because it results in an additional large loss of the entropy of the redistribution of low-molecular charges (counterions and salts), needed for the compensation of the polymer charge. This is why under certain conditions the competition between the short-range segregating and Coulomb stabilizing interactions in polyelectrolyte solutions may give rise to structural phase transitions of the weak crystallization type.

We shall consider these phase transitions and equilibria of the corresponding phases in the following sequence. In Sec. 2 we present a general method for the derivation of the appropriate Hamiltonian and its reduction to the Landau–Brazovskiĭ (LB) form in the specific example of one simple polyelectrolyte system. In Sec. 3 we give an additional formulation of the Brazovskiĭ approximation based on the use of the variational principle, which is convenient for the calculation of the correlation functions and the free energy of such systems which are described by that Hamiltonian for which the quantities $q_0$, $\gamma$, and $\lambda$ differ for the coexisting phases. The results obtained are used in Sec. 4 to construct and analyze the phase diagram of the investigated system both in the mean-field and Brazovskiĭ approximations, and to demonstrate that supercrystalline phases exist and can coexist with one another and with liquid phases. Finally, in Sec. 5 we discuss the conditions for selection of real polymer systems which can exhibit the phase diagram in question.

## 2. CONTINUUM DESCRIPTION AND THE LANDAU-BRAZOVSKII HAMILTONIAN OF POLYELECTROLYTE SYSTEMS

Consider a system in which there are on the average $N_s$ (macro)molecules of type $S$ in volume $V$ (the type of molecules may be described by their structure formulas). In order to describe the state of such a system we have to specify not only molecular-structure distribution $\{N_s\}$, but also the distribution in the space of local densities (numbers per unit volume) $\{\rho_i(\mathbf{r})\}$ of all $k$ types of particles or "broken links" (see below) in the system. (We regard as particles both the links in the macromolecules and small molecules which may differ from one another by the nature of the short-range interparticle interaction and have a charge $z_i e$, where $e$ is the electron charge and $z_i$ is the valence of particles of type $i$.) The free energy of such a system can be represented by the functional integral over the densities $\{\rho_i(\mathbf{r})\}$:

$$F=-T\ln\int\delta\rho_i(\mathbf{r})\exp\{-F(\{\rho_i(\mathbf{r})\},T)/T\}, \tag{1}$$

which can be given a rigorous meaning by the method of collective variables,[16] and in our case it is convenient to carry out calculations by a method described in Ref. 9 and including a procedure for the removal of ultraviolet divergences typical of systems with the Coulomb interaction[13] and of polymer systems with a local interaction between links.[17,18] The quantity $F(\{\rho_i(\mathbf{r})\},T)$ in Eq. (1) is the free energy of such a polymer system with a specified (nonequilibrium) distribution of the densities $\{\rho_i(\mathbf{r})\}$, which can be represented in the form

$$F(\{\rho_i(\mathbf{r})\},T)=\tilde{F}(\{\rho_i(\mathbf{r})\},T)+\int d\mathbf{r}\,d\mathbf{r}'\,\frac{Q(\mathbf{r})Q(\mathbf{r}')}{\varepsilon|\mathbf{r}-\mathbf{r}'|}. \tag{2}$$

Here, $Q(\mathbf{r}) = e\Sigma z_i\rho_i(\mathbf{r})$ is the local charge of the system, $\varepsilon$ is the permittivity of the medium, $e$ is the electron charge, and $\tilde{F}(\{\rho_i(\mathbf{r})\}, T)$ is the free energy of what is known as the basis system[9,11,16] whose polymer structure and the short-range interaction between the particles are exactly the same as for the investigated polyelectrolyte, but all the valences $z_i$ become zero.

We now calculate the functional integral (1) by expanding the free energy $F(\{\rho_i(\mathbf{r})\}, T)$ as a series in the postulated small fluctuations

$$\Phi_i(\mathbf{r})=\rho_i(\mathbf{r})-\bar{\rho}_i\quad\left(\bar{\rho}_i=V^{-1}\int d\mathbf{r}\,\rho_i(\mathbf{r})\right), \tag{3}$$

retaining, as is usual in the Landau theory of second-order phase transitions,[13] only terms up to fourth order in $\Phi_i(\mathbf{r})$:

$$F(\{\rho_i(\mathbf{r})\},T)=F_0(\{\bar{\rho}_i\},T)+\sum_{n=2}^{4}(\Gamma^{(n)}\Phi^n)/n!, \tag{4}$$

where the following notation is used:

$$(\Gamma^{(n)}\Phi^n)=\sum_{\{\alpha_1,\ldots,\alpha_n\}}\int\Gamma^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{r}_1,\ldots,\mathbf{r}_n)\prod_{i=1}^{n}\Phi_{\alpha_i}(\mathbf{r}_i)\,d\mathbf{r}_i, \tag{5}$$

$$(\gamma^{(n)}\varphi^n)=\sum_{\{\alpha_1,\ldots,\alpha_n\}}\int\gamma^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1\ldots\mathbf{q}_n)\prod_{i=1}^{n}\varphi_{\alpha_i}(\mathbf{q}_i)\frac{d\mathbf{q}_i}{(2\pi)^3},$$

$$\Gamma^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{r}_1,\ldots,\mathbf{r}_n)=\delta^nF(\{\rho_i(\mathbf{r})\},T)/\delta\rho_{\alpha_1}(\mathbf{r}_1)\ldots\delta\rho_{\alpha_n}(\mathbf{r}_n),$$

$$\gamma^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{q}_1,\ldots,\mathbf{q}_n)=\int\Gamma^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{r}_1,\ldots,\mathbf{r}_n)\prod_{i=1}^{n}\exp(i\mathbf{q}_i\mathbf{r}_i)\,d\mathbf{r}_i. \tag{5a}$$

The integration with respect to each of the coordinates $\mathbf{r}_i$ in Eq. (5) is carried out over the whole volume $V$ of the system and the summation (instead of the summation sign we shall use the Einstein rule for the summation with repeated indices: $\Sigma_{i=1}^{k} u_i v_i = u_i v_i$) is carried out over all the transpositions $(\alpha_1,\ldots,\alpha_n)$ of $n$ (not necessarily different) numbers $\alpha_i$ each of which can have any value from unity to $k$, where $k$ is the total number of different types of particles of the investigated polymer system or, which is equivalent, the number of components of the corresponding system of broken links.

The concept of a system of broken links introduced by Lifshitz[19] makes it possible to obtain explicit expressions for the vertex functions $\Gamma^{(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$ in terms of the microscopic characteristics of the interparticle interaction and the polymer structure, bearing in mind the following considerations. This concept is valid in the case of (not very dilute) polymer systems for which the main contribution to the interaction energy comes from collisions between links belonging to different micromolecules. Averaging of the contribution of these collisions which occur over short (low-molecular) distances can be made statistically independently of averaging of the contribution of the conformation set of macromolecules, which occur at longer (macromolecular) distances. (The condition for the validity of the factorization of these averages and, therefore, the validity of the idea of a system of broken links and the more general concept of a system of "quasimonomers"[20] are discussed in Ref. 21.) Therefore, the partition function of such systems splits into a product and the free energy into a sum of the corresponding contributions:

$$F(\{\rho_i(\mathbf{r})\}, T)=F^*(\{\rho_i(\mathbf{r})\}, T)+F_s(\{\rho_i(\mathbf{r})\}, \{N_S\}, T), \tag{6}$$

where the first (energy) term, which in view of the above is independent of the polymer structure, can be interpreted as the contribution of the free energy $F$ of some model low-molecular system representing broken links. (The quantity $F^*$ is frequently called the contribution of the bulk interaction between the polymer links.) In the case of the structure-entropy contribution $F_s(\{\rho_i(\mathbf{r})\}, \{N_s\}), T$, it represents the free energy of an ideal polymer, i.e., of a system of noninteracting (macro)molecules (including the small molecules of the solvent) with the same molecular-structure distribution $\{N_s\}$ as in the case of the polymer system of interest.

In particular, instead of $F^*(\{\rho_i(\mathbf{r})\}, T)$, it is frequently convenient to use an expression obtained using the Flory–Huggins lattice model, which is standard in the theory of polymers:[17,18,22,23]

$$F^*(\{\rho_i(\mathbf{r})\}, T)=-\frac{1}{2}\int dV v_{ij}\rho_i(\mathbf{r})\rho_j(\mathbf{r}), \tag{7}$$

where $v_{ij}$ is the matrix describing the bulk interaction between the particles in a melt. Equation (7) describes only that part of the bulk interaction which corresponds to the attraction between particles, whereas the presence of a solid core (excluded volume) of the particles is allowed for by adding the condition of incompressibility which imposes limitations on possible local fluctuations of the melt composition:

$$\sum v_i\rho_i(\mathbf{r})=1, \tag{8}$$

where $v_i$ is the excluded volume of particles of type $i$. Therefore, in this case, which is the only one which we shall consider, we have

$$\Gamma_{ij}^{*(2)}(\mathbf{q})=-v_{ij},$$

and if $n>2$, then all the coefficients $\Gamma^{*(n)}_{\alpha_1\ldots\alpha_n}(\mathbf{r}_1,\ldots,\mathbf{r}_n)$ vanish identically [here and later an appropriate index will be used to denote that part of the functional derivative of Eq. (5a) which is taken from the contribution with the same index].

However, in a calculation of the polymer contribution it is convenient to employ the familiar interpolation expression for the free energy $F_s(\{\rho_i(\mathbf{r})\}, \{N_s\}, T)$ of an ideal polymer mixture suitable in the case when the characteristic scale of fluctuations is small compared with the dimensions of a polymer tangle, as well as in the opposite limiting case:[17,22]

$$F_s(\{\rho_i(\mathbf{r})\},\{N_S\},T)=T\sum_k\int dV\rho_k(\mathbf{r})\ln\frac{\rho_k(\mathbf{r})}{e}$$
$$+T\sum_S\int dV\left\{\frac{\bar\rho_S}{N_S}\ln\bar\rho_S+\frac{a^2}{6}[\nabla(\rho_S(\mathbf{r}))^{1/2}]^2\right\}. \tag{9}$$

The summation in the first term of Eq. (9) is carried out over all types of low-molecular components (i.e., counterions, salts, and possibly solvents); in the second term it is carried out over all the macromolecules of the system with the structure formula $S$; $a$ is the size of a statistical segment; $\bar\rho_s$ is the average density of macromolecules of type $S$. Using Eqs. (7) and (9) in writing down Eq. (6) and substituting then Eq. (6) into Eq. (2), we readily obtain the final expression for the coefficients in the expansion of the free energy of a polyelectrolyte system in terms of the density fluctuations.

However, it is pointless to write down this expression for polydisperse polyelectrolyte systems in its general form, because of the difficulty of analyzing the phase diagrams of systems with a large number of thermodynamic degrees of freedom when several phases may coexist, when there may be triple points, etc. (A similar situation is encountered also in the case of heteropolymers with more than two components.) Therefore, in the present investigation we analyze the conditions of formation of a domain structure and the nature of a typical phase diagram by using the following simple model, proposed in Ref. 14, with just one thermodynamic degree of freedom. We discuss a polymer melt consisting of a polyelectrolyte $A$ containing (on the average) one charged group for every $m$ monomer links, and an uncharged polymer $B$ with the degrees of polarization $N_A$ and $N_B$, respectively, and we assume that the average concentration of the polyelectrolyte is

$$\bar\rho_A=\nu_AN_A/(\nu_AN_A+\nu_BN_B),$$

where $\nu_i$ is the average number of macromolecules of type $i$ per unit volume. We also assume that the excluded volumes of the charged and uncharged links $A$ and $B$ are equal for the same value of $v$, while the salt effects can be ignored, since counterions present of necessity in the system for the purpose of neutralizing the polymer charge and assumed (for the sake of simplicity) to have the same valence $z$ as the charged links of the polymer $A$, contribute only to the Coulomb interaction and their contribution to the bulk interaction can be ignored (the error committed by this assumption is of order $1/m$, i.e., it is small for the present case of a weakly charged polyelectrolyte characterized by $m\gg1$). Then, the condition of incompressibility (8) can be written in the form

$$x_A(\mathbf{r})+x_B(\mathbf{r})=1, \tag{8a}$$

where $x_i(\mathbf{r})=v\rho_i(\mathbf{r})$ is the volume fraction of a polymer of type $i$ at the point $\mathbf{r}$. Therefore, the state of the system in question is characterized by a distribution of two independent local densities: the density $\rho_A(\mathbf{r})$ of all (charged or uncharged) links in a weakly charged polyelectrolyte [or their volume fraction $x_A(\mathbf{r})$] and the density of counterions $\rho_c(\mathbf{r})$. In contrast to the local condition of incompressibility of Eq. (8a), the condition for electrical neutrality of this system as a whole

$$\bar\rho_c=\frac{1}{V}\int d\mathbf{r}\rho_c(\mathbf{r})=\frac{\bar\rho_A}{m}=\frac{1}{mV}\int d\mathbf{r}\,\rho_A(\mathbf{r})$$

does not affect the independence of the Fourier components of the corresponding densities

$$\varphi_i(\mathbf{q})=\int dV\rho_i(\mathbf{r})\exp(i\mathbf{q}\mathbf{r})$$

when $q=0$. On the other hand, $\bar x_A=v\bar\rho_A$ is the only thermodynamic parameter which represents the state of the system as a whole.

On this basis we can write down the following expression for the free energy of the investigated system:

$$\frac{F(\{\rho_i(\mathbf{r})\},T)}{T}=\int dV\rho_2(\mathbf{r})\ln\frac{\rho_2(\mathbf{r})}{e}+\frac{V}{v}\left[\frac{\bar{x}_1\ln\bar{x}_1}{N_A}+\frac{(1-\bar{x}_1)\ln(1-\bar{x}_1)}{N_B}+\chi\bar{x}_1(1-\bar{x}_1)\right]$$
$$+\frac{a^2}{24v}\int dV\frac{[\nabla x_1(\mathbf{r})]^2}{x_1(\mathbf{r})[1-x_1(\mathbf{r})]}$$
$$+l_b z_i z_j\int d\mathbf{r}\,d\mathbf{r}'\frac{\rho_i(\mathbf{r})\rho_j(\mathbf{r}')}{4\pi|\mathbf{r}-\mathbf{r}'|}, \tag{10}$$

where $\chi=(v_{aa}+v_{bb}-2v_{ab})/2vT$ is what is known as the Flory–Huggins parameter representing the short-range interaction between the links $A$ and $B$ (Refs. 17, 18, 22, and 23), which is usually represented in the form $\chi=\Theta/2T$ (the quantity $\Theta$ is known as the Flory temperature) and $l_b=4\pi e^2/\varepsilon T$ is known as the Bjerrum length. In Eq. (10) and in the following text the indices 1 and 2 denote the densities of all (both charged and uncharged) links in a polyelectrolyte and counterions. In accordance with the definition of our system, we have $z_2=z$ and $z_1=z/m$, since in this case the correlation radius (or, which is equivalent, the screening radius) of the system under consideration is large compared with the rms distance between the charged links of a polymer (this is the case which is attracting most interest), so that a polyelectrolyte can be regarded as uniformly charged with an average linear charge density $ze/m$ per polymer link. The quantities which then occur in the expansion (4) of the functional (10) are given by the following expressions

$$\frac{F_0(\{\bar{\rho}_i\},T)}{T}$$
$$=\left(\frac{V}{v}\right)\left(\frac{\bar{x}_A\ln\bar{x}_A}{N_A}+\frac{\bar{x}_B\ln\bar{x}_B}{N_B}+\chi\bar{x}_A\bar{x}_B+\frac{\bar{x}_A}{m}\ln\frac{\bar{x}_B}{m}\right),$$
$$\Gamma_{ij}^{(2)}(\mathbf{q})=\tilde{\Gamma}_{ij}^{(2)}(\mathbf{q})+l_b z_i z_j/\mathbf{q}^2,$$
$$\tilde{\Gamma}_{11}^{(2)}(\mathbf{q})=v\{(\mathbf{q}a)^2/(12\bar{x}_A\bar{x}_B)-2\chi\},$$
$$\tilde{\Gamma}_{22}^{(2)}(\mathbf{q})=mv/\bar{x}_A,\quad \tilde{\Gamma}_{12}^{(2)}(\mathbf{q})=\tilde{\Gamma}_{21}^{(2)}(\mathbf{q})=0,$$
$$\Gamma_{111}^{(3)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3)=-v^2\frac{\bar{x}_A-\bar{x}_B}{(\bar{x}_A\bar{x}_B)^2}\frac{(\mathbf{q}_1^2+\mathbf{q}_2^2+\mathbf{q}_3^2)a^2}{24},$$
$$\Gamma_{1111}^{(4)}(\mathbf{q}_1,\mathbf{q}_2,\mathbf{q}_3,\mathbf{q}_4)=v^3\left(\frac{1-3\bar{x}_A\bar{x}_B}{(\bar{x}_A\bar{x}_B)^3}\right)\frac{(\mathbf{q}_1^2+\mathbf{q}_2^2+\mathbf{q}_3^2+\mathbf{q}_4^2)a^2}{12},$$
$$\Gamma_{2\ldots2}^{(n)}=(-1)^n(n-2)!/(mv/\bar{x}_A)^{n-2}. \tag{11}$$

Before we investigate the conditions of formation of the supercrystalline order in our system, we have to face the question of selection of the order parameter in order to describe the effect. Usually second-order phase transitions are described selecting as the order parameter that variable or combination of variables which fluctuates most strongly as the phase transition point is approached (in general, the phase transition surface).[24] Consequently, in our case we have to investigate the eigenvalues $\{\lambda_i(\mathbf{q})\}$ of the inverse matrix of the total density–density correlation functions $\mathcal{G}^{-1}(\mathbf{q})$:

$$\mathcal{G}^{-1}(\mathbf{q})=\|\Gamma_{ij}^{(2)}(\mathbf{q})\|. \tag{12}$$

Obviously, the system may be in a spatially homogeneous state (even metastable) only if the matrix $\mathcal{G}^{-1}(\mathbf{q})$ is positive definite. Therefore, the point (or in general the surface of the spinodal) which limits the range of the absolute instability of a spatially homogeneous state of the system is described by the condition

$$\min\lambda_-(q)=0, \tag{13}$$

where $\lambda_-(q)$ is the minimum, for a given value of $q$, eigenvalue of the matrix $\mathcal{G}^{-1}(q)$ and the minimum of Eq. (13) is sought on the semiaxis $0\leqslant q^2\leqslant\infty$. Two cases are possible: 1) if the minimum of Eq. (13) occurs at $q_0=0$, then for $\lambda_-(q_0)<0$ we have the usual stratification due to macroscopic spatially homogeneous phases; 2) if the minimum (13) is reached at $q_0\neq0$, then for $\lambda_-(q_0)<0$ the supercrystalline order appears in the system. In both cases the role of the order parameter is played by the eigenvector which corresponds to the eigenvalue $\lambda_-(q_0)<0$.

If we consider the term with the Coulomb interaction as a regular perturbation,[25] we readily obtain the following expression for the eigenvalues of the matrix (12):

$$1+\frac{\varkappa}{(qa)^2}\left(\frac{z_1^2}{\lambda_1^0-\lambda}+\frac{z_2^2}{\lambda_2^0-\lambda}\right)=0, \tag{14}$$

where $\lambda_1^0(q)=\tilde{\Gamma}_{11}(\mathbf{q})/v$, $\lambda_2^0=\tilde{\Gamma}_{22}/v$, $\varkappa=l_b a^2/v$. We can easily see that the larger of these eigenvalues is always positive, whereas the smaller tends to zero, which can be described by a fraction

$$\lambda_-(q)$$
$$=-\left\{(qa)^2+\varkappa\left(\frac{z_1^2}{\lambda_1^0}+\frac{z_2^2}{\lambda_2^0}\right)\right\}\left\{\varkappa\left[\frac{z_1^2}{(\lambda_1^0)^2}+\frac{z_2^2}{(\lambda_2^0)^2}\right]\right\}^{-1}.$$

Therefore, the solution of Eq. (13) is obtained when the value of the numerator of this fraction

$$D(q)=(qa)^2+\varkappa\left[\frac{(z/m)^2}{(qa)^2/(12\bar{x}_A\bar{x}_B)-2\chi}+\frac{z^2\bar{x}_A}{m}\right]$$

and its derivative with respect to $q$ vanish simultaneously,[9,11] which gives rise to the expressions obtained in Ref. 14 for the equation of the spinodal (boundary of the region of the absolute instability of a spatially homogeneous state, which may be even metastable) and the critical momentum of the investigated system:

$$\tilde{\chi}=\left(\frac{\varkappa}{12\bar{x}_A\bar{x}_B}\right)^{1/2}-\frac{\varkappa}{24\bar{x}_B}, \tag{15a}$$

$$q_*^2a^2=\left[2\tilde{\chi}-\left(\frac{\varkappa}{12\bar{x}_A\bar{x}_B}\right)^{1/2}\right]\frac{12\bar{x}_A\bar{x}_B}{m}, \tag{15b}$$

where $\tilde{\chi}=\chi^m$. In standardization of these equations and reduction of our effective Hamiltonian to the Landau–Brazovskiĭ Hamiltonian, it is convenient to introduce new dimensionless quantities:[9,11]

$$Q_*^2=q_*^2a^2r_p^2,\quad r_p^2=m/(12\varkappa\bar{x}_A\bar{x}_B)^{1/2},\quad \varkappa=l_ba^2/v,$$
$$s=\bar{x}_AI,\quad t=-2\tilde{\chi}/I,\quad I=(\varkappa/12\bar{x}_A\bar{x}_B)^{1/2}. \tag{16}$$

We can easily show that if we use such notation, then the solution of Eq. (15) and the tangent of the angle $\alpha(q)$, which determines the transition to the basis of the eigenvectors $\Psi_i$ of the matrix (12) by the transformations

$$\varphi_1(q)=\Psi_1(q)\cos\alpha(q)-\Psi_2(q)\sin\alpha(q),$$

$$\varphi_2(q)=\Psi_1(q)\sin\alpha(q)+\Psi_2(q)\cos\alpha(q),$$

can be written in the following simple form:

$$t=s-2, \tag{17a}$$

$$Q_*^2=1-s, \tag{17b}$$

$$\mathrm{tg}[2\alpha(q_0)]=\frac{2\varkappa}{m(q_*a)^2[\Gamma_{22}(q_*)-\Gamma_{11}(q_*)]}=\frac{2}{m}\frac{s^{1/2}}{1-s^{1/2}}+o(m^{-2}). \tag{18}$$

Therefore, an instability typical of the weak crystallization process occurs in the case of a finite value of the critical momentum $Q_*^2>0$ only if the condition $s<1$ is satisfied. Not too close to the boundary of the region within which weak crystallization exists, as demonstrated by Eq. (18), we have $\mathrm{tg}[2\alpha(q_0)]\to 0$ when $m\to\infty$. In other words, for weakly charged polyelectrolytes in the region where supercrystalline phases can exist, we can assume that a strongly fluctuating order parameter $\Psi_1(\mathbf{q})$ is proportional to fluctuations of the polyelectrolyte density $\rho_1(\mathbf{q})$, while the weakly fluctuating order parameter $\Psi_2(\mathbf{q})$ is proportional to fluctuations of the counterion density $\rho_2(\mathbf{q})$. Therefore, in carrying out the preliminary integration over all the distributions of the counterion density in the continuum integral (1) needed to obtain the effective Hamiltonian as a functional of just the strongly fluctuating order parameter, we can limit ourselves to the single-loop approximation, corresponding to the Debye–Hückel theory, which allows us to write the free energy of Eq. (1) in the form

$$F=\tilde{F}_0(\bar{x}_A,T)+\Delta F,$$

$$\Delta F=-T\ln\int\delta\rho_1(\mathbf{r})\exp\{-\Delta F(\{\rho_1(\mathbf{r})\},T)/T\}, \tag{1a}$$

where

$$\frac{\tilde{F}_0(\bar{x}_A,T)}{T}=\frac{V}{v}\left(\frac{\bar{x}_A\ln\bar{x}_A}{N_A}+\frac{\bar{x}_B\ln\bar{x}_B}{N_B}+\frac{\bar{x}_A}{m}\ln\frac{\bar{x}_A}{m}+\chi\bar{x}_A\bar{x}_B-\frac{1}{12\pi}\frac{v}{a^3}\left(\frac{\varkappa\bar{x}_A}{m}\right)^{3/2}\right), \tag{19}$$

and the continuum integral describing the fluctuation contribution to the free energy can be rewritten conveniently by using the variables (16) introduced above and substituting the integration variable

$$\Psi^2(\mathbf{Q})=\frac{4\mathrm{v}IQ_*^2}{a^3mr_p{}^3}\varphi^2(\mathbf{q}), \tag{20}$$

in the following way:

$$\Delta F=-T\ln\int\delta\Psi(\mathbf{r})\exp\{-H(\{\Psi(\mathbf{r})\},T)/T\},$$

$$H(\{\Psi(\mathbf{Q})\},T)=\frac{1}{2!}\int\frac{g^{-1}(\mathbf{Q})\Psi(\mathbf{Q})\Psi(-\mathbf{Q})}{4Q_*^2}\frac{d\mathbf{Q}^3}{(2\pi)^3}+\ldots, \tag{21}$$

where

$$g^{-1}(\mathbf{Q})=\gamma^{(2)}(\mathbf{Q})=\mathbf{Q}^2+t+(\mathbf{Q}^2+s)^{-1}. \tag{22}$$

Since $g^{-1}(Q)$ considered as a function of $Q=|\mathbf{Q}|$ has a minimum at $Q=Q_*=(1-s)^{1/2}$, it can be expanded near this minimum as a Taylor series in powers of $(Q-Q_*)$:

$$g^{-1}(Q)=(2\ Q_*)^2\{\tau+(Q-Q_*)^2+\ldots\}, \tag{23}$$

where $4\tau=(2-s+t)/(1-s)$ and the leading terms of the expansion (23) in the range $\tau/Q_*^2\ll 1$, typical of the weak crystallization region, can be ignored. Moreover, since in the case of the correlation function of the (23) type the main contribution to the calculation of the diagrams is made by momenta close to $Q_*$ in magnitude, we must assume

$$\gamma(Q_1,Q_2,Q_3)\approx\gamma(Q_*,Q_*,Q_*)=\gamma,$$

$$\lambda(Q_1,Q_2,Q_3,Q_4)=\lambda(Q_*,Q_*,Q_*,Q_*)=\lambda.$$

Next, substituting Eq. (23) into Eq. (21) and making the substitutions indicated above, we finally obtain an expression which is fully identical with the Landau–Brazovskiĭ Hamiltonian:

$$\Delta F(\{\Psi(\mathbf{Q})\},T)=\frac{1}{2}\int((|\mathbf{Q}|-Q_*)^2+\tau)\Psi(\mathbf{Q})\Psi(-\mathbf{Q})\frac{d\mathbf{Q}}{(2\pi)^3}-\frac{\tilde{\gamma}}{3!}\int\delta(\mathbf{Q}_1+\mathbf{Q}_2+\mathbf{Q}_3)\prod_{i=1}^{3}\Psi(\mathbf{Q}_i)\frac{d\mathbf{Q}_i}{(2\pi)^3}+\frac{\tilde{\lambda}}{4!}\int\delta(\mathbf{Q}_1+\mathbf{Q}_2+\mathbf{Q}_3+\mathbf{Q}_4)\times\prod_{i=1}^{4}\Psi(\mathbf{Q}_i)\frac{d\mathbf{Q}_i}{(2\pi)^3}, \tag{24}$$

where

$$\tilde{\gamma}=(\bar{x}_A-\bar{x}_B)(3^{1/2}/2)^3\alpha,\qquad\tilde{\lambda}=3[1-3(\bar{x}_A\bar{x}_B)]\alpha^2,$$

$$\alpha=(v/a^3m^{1/2})^{1/2}(12\varkappa/(\bar{x}_A\bar{x}_B)^3)^{1/8}Q_*^{-1}. \tag{25}$$

## 3. VARIATIONAL PRINCIPLE AND CALCULATION OF THE FLUCTUATION CORRECTIONS TO THE FREE ENERGY OF THE HAMILTONIAN OF THE LANDAU–BRAZOVSKIĬ TYPE

In the calculations of the contribution $\Delta F$ to the total free energy of the system made using the mean field approximation, i.e., accurate to within a preexponential factor, it is sufficient to find a minimum of the functional (24) which should be found assuming $\tau<0$—i.e., in the instability range of a spatially homogeneous (liquid) state—using the theory of weak crystallization and seeking the class of nonzero periodic functions of the coordinate $\Psi(\mathbf{r})$ with the symmetry of some Bravais lattice:

$$\Psi(\mathbf{r})=\sum_{\mathbf{q}}A(\mathbf{q})\exp(i\mathbf{q}\mathbf{r}), \tag{26}$$

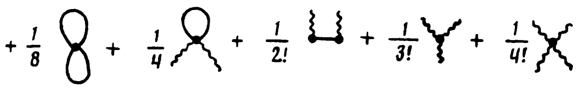
where the summation is carried out over all the vectors of the reciprocal lattice (related to the corresponding Bravais lattice) whose absolute values are $Q_*$.

A correct allowance for fluctuation effects, i.e., calculation of the integral (22) in the situation when the corrections to the steepest-descent value of this integral are large, must include the transition from the unrenormalized (bare) correlation functions (in our case they are the density–density correlation functions) to the total (renormalized allowing for the fluctuations) correlation functions. This transition is easily made using the general field approach[26] based on derivation of the generating functional of the appropriate class of diagrams in which the arguments are both the unrenormalized and total correlation functions. The free energy of the system is then found by minimizing this functional with respect to the total correlation functions and the dependence of these functions on the parameters of the system (temperature and composition) is obtained by solving the appropriate equations for extremals. In the theory of weak crystallization it is quite permissible, as demonstrated by Brazovskiĭ,[3] to allow only for the influence of fluctuations on the renormalization of a pair correlation function, so that the renormalized pair correlation function is sought in the form

$$G^{-1}(Q)=(|\mathbf{Q}|-Q_*)^2+r. \qquad (27)$$

Omitting the intermediate steps, corresponding to what is known as the second Legendre transformation,[26] we give the final expression for the free energy in the form of the following functional series:

$$\frac{\Delta F(\{\rho_i\},T)}{T}=-\frac{1}{2}\operatorname{Sp}\ln G(\mathbf{r}_1-\mathbf{r}_2)+\frac{1}{2}\int\{g^{-1}(\mathbf{r}_1-\mathbf{r}_2)$$
$$-G^{-1}(\mathbf{r}_1-\mathbf{r}_2)\}G(\mathbf{r}_2-\mathbf{r}_1)d\mathbf{r}_1\,d\mathbf{r}_2$$



$$=\frac{1}{2}\left\{\int\{g^{-1}(\mathbf{r}_1-\mathbf{r}_2)-G^{-1}(\mathbf{r}_1-\mathbf{r}_2)\}\right.$$
$$\left.\times G(\mathbf{r}_2-\mathbf{r}_1)d\mathbf{r}_1\,d\mathbf{r}_2-\operatorname{Sp}\ln G(\mathbf{r}_1-\mathbf{r}_2)\right\}$$
$$+\frac{1}{8}\int\lambda(\mathbf{r}_1,\ldots,\mathbf{r}_4)G(\mathbf{r}_1-\mathbf{r}_2)G(\mathbf{r}_3-\mathbf{r}_4)\prod_{i=1}^{4}d\mathbf{r}_i$$
$$+\frac{1}{4}\int\lambda(\mathbf{r}_1,\ldots,\mathbf{r}_4)G(\mathbf{r}_1-\mathbf{r}_2)\Psi(\mathbf{r}_3)\Psi(\mathbf{r}_4)\prod_{i=1}^{4}d\mathbf{r}_i$$
$$+\frac{1}{2}\int\Psi(\mathbf{r}_1)g^{-1}(\mathbf{r}_1-\mathbf{r}_2)\Psi(\mathbf{r}_2)d\mathbf{r}_1\,d\mathbf{r}_2+\frac{1}{3!}\int\gamma(\mathbf{r}_1,\ldots,\mathbf{r}_3)$$
$$\times\prod_{i=1}^{3}\Psi(\mathbf{r}_i)d\mathbf{r}_i+\frac{1}{4!}\int\lambda(\mathbf{r}_1,\ldots,\mathbf{r}_4)\prod_{i=1}^{4}\Psi(\mathbf{r}_i)d\mathbf{r}_i+\ldots, \qquad (28)$$

which includes expressions only for the contributions of those diagrams which correspond to the Brazovskiĭ approximation, while the contributions of higher-order diagrams corresponding to the renormalization of the vertices of the third and fourth orders are omitted, which is permissible if

$$\tilde{\gamma}^2/Q_*\tilde{\lambda}r^{1/2}\ll 1, \qquad \tilde{\lambda}Q_*/24r\ll 1.$$

Then the Brazovskiĭ approximation itself has the following range of validity[3]

$$(\tilde{\gamma}^2/Q_*^2\tilde{\lambda})^3\ll\tilde{\lambda}/Q_*\ll 1. \qquad (29)$$

Replacing $g$, $G$, and $\Psi$ in Eq. (28) with the expressions (23), (27), and (26), we obtain

$$\Delta F_n(\{\rho_i\},T)=\frac{VT}{r_p{}^3}\left(\frac{1}{2}hr^{1/2}+\frac{1}{2}\frac{h\tau}{r^{1/2}}+\frac{1}{8}\frac{h^2\tilde{\lambda}}{r}\right.$$
$$\left.+\frac{1}{2}\frac{h\tilde{\lambda}A^2}{r^{1/2}}+\tau A^2-\alpha_nA^3+\beta_nA^4\right), \qquad (30)$$

where $h=Q_*^2/2\pi$, $A$ are identical—as demonstrated by direct minimization of similar functionals in Refs. 2–4 and 6—amplitudes of the reciprocal lattice vectors belonging to the first coordination sphere, and the coefficients $\alpha_n$ and $\beta_n$ depend on the nature of the supercrystalline lattice as follows:

for a lamellar lattice (l)

$$\alpha_1=0, \quad \beta_1=\tilde{\lambda}/4,$$

for a triangular ($\Delta$) lattice

$$\alpha_3=2\tilde{\gamma}/3^{3/2}, \quad \beta_3=5\tilde{\lambda}/12,$$

for a body-centered (bcc) lattice

$$\alpha_6=4\tilde{\gamma}/(3\cdot 6^{1/2}), \quad \beta_6=15\tilde{\lambda}/24.$$

Minimization of the functions (30) with respect to $r$ and $A$ gives a system of equations first obtained by Brazovskiĭ;[3] this system of equations defines $r$ and $A$ as functions of the effective temperature $\tau$ and characterizes the form of the supercrystalline lattice by the parameters $\alpha_n$ and $\beta_n$:

$$r-\tau-h\tilde{\lambda}/2r^{1/2}-\tilde{\lambda}A^2=0,$$
$$A(h\tilde{\lambda}/r^{1/2}+2\tau-3\alpha_nA+4\beta_nA^2)=0. \qquad (31)$$

Therefore, the variational principle based on minimization of the functional (28) gives an alternative formulation of the theory of Refs. 3 and 4. It is specifically in the case of this formulation that the theory of weak crystallization is more suitable for describing the formation of a domain structure in systems in which $\tau, \gamma, \tilde{\lambda}, Q_*$ are functions of the state of the system or, as in our case, depend on the composition of the melt. This is because the method for the calculation of the free energies of the supercrystalline phases proposed in Refs. 3 and 4 makes it possible to find only the differences between these energies and the free energy of a homogeneous state with the same values of the parameters $\tau, \tilde{\gamma}, \tilde{\lambda}, Q_*$, which is undoubtedly fully justified and convenient in an investigation of the phase transitions in systems for which these parameters are the same for all the coexisting phases. However, as shown in the preceding section, in our case these parameters clearly depend on the volume fraction of a polyelectrolyte and stratification of the latter should make them different for the coexisting phases. Therefore, in discussing the equilibria of the phases (for example, supercrystalline) in polyelectrolyte systems we must know the absolute value of the free energy, which (in contrast to Refs. 3 and 4) allows us to find the functional (28).

Substituting in Eq. (31) the trivial solution $A=0$, which corresponds to a homogeneous phase, we can find the dependence of $r$ on $\tau$ for the homogeneous phase:

$$r=\tau+h\tilde{\lambda}/2r^{1/2}. \tag{32}$$

However, in the case of an inhomogeneous state we have to solve the system

$$\begin{aligned} &r-\tau-h\tilde{\lambda}/2r^{1/2}-\tilde{\lambda}A^2=0,\\ &h\tilde{\lambda}/r^{1/2}+2\tau-3\alpha_nA+4\beta_nA^2=0. \end{aligned} \tag{33}$$

Substitution in Eq. (30) of the solutions of Eq. (32) or of the system (33) for different types of lattices yields the dependence $\Delta F_n(\{\rho_i(\mathbf{r})\}, T)$ for a supercrystalline state of a given symmetry on the temperature and composition of the polyelectrolyte. Similar expressions, defining $r$ and $\Delta F_n(\{\rho_i(\mathbf{r})\}, T)$ are obtained in the mean field approximation if Eq. (30) is simplified by dropping terms of the $h\tilde{\lambda}/r^{1/2}$ type, which corresponds to assuming that the perturbation parameter $h\tilde{\lambda}/r^{3/2}$ is small.

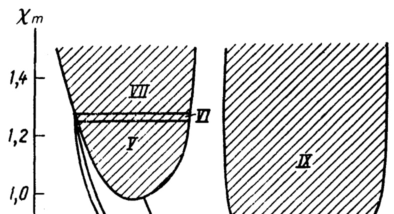


FIG. 2. Phase diagram of the investigated polymer system calculated in the mean-field approximation assuming that $\varkappa = 1$. The shaded regions represent coexistence of two phases. The regions are numbered as follows: I) L; II) bcc; III) Δ; IV) l; V) Δ-$l_1$; VI) bcc-$l_1$; VII) $L_1$-$l_1$; VIII) $\Delta_2$-$L_2$ and bcc-$\Delta_2$; IX) $L_2$-$l_2$.

## 4. PHASE DIAGRAMS OF THE INVESTIGATED POLYELECTROLYTE SYSTEM

We now describe the procedure for constructing the phase diagram of the investigated polyelectrolyte system. With this in mind we write down the final expression for the free energy, which is found by combining Eqs. (17) and (28):

$$\begin{aligned} F_n(\{\rho_i\}, T)=\frac{TV}{v}\Bigg\{&\frac{\bar{x}_A\ln\bar{x}_A}{N_A}+\frac{(1-\bar{x}_A)\ln(1-\bar{x}_A)}{N_B}+\frac{\bar{x}_A\ln\bar{x}_A}{m}\\ &+\chi\bar{x}_A\bar{x}_B-\frac{1}{12\pi}\frac{v}{a^3}\left(\frac{\varkappa\bar{x}_A}{m}\right)^{3/2}+\frac{v}{r_p{}^3}\Bigg\{\frac{1}{2}hr^{1/2}\\ &+\frac{1}{2}\frac{h\tau}{r^{1/2}}+\frac{1}{8}\frac{h^2\tilde{\lambda}}{r}+\frac{1}{2}\frac{h\tilde{\lambda}A^2}{r^{1/2}}+\tau A^2-\alpha_nA^3+\beta_nA^4\Bigg\}\Bigg\}, \end{aligned} \tag{34}$$

where the equilibrium values of $r$ and $A$ for a given supercrystalline phase are found, as described in the preceding section, by minimization of the function (34) with respect to these quantities, while $n$ is used to number the type of the supercrystalline lattice. Determination of the metastable regions is carried out in the usual way and in general the boundaries of these regions need not coincide with the boundaries of similar regions for a homogeneous melt. The equilibrium compositions of the phases for a fixed type of supercrystalline lattice symmetry should be sought either by solving the system of equations assuming the equality of the pressures and chemical potentials of the stratified phases or by directly minimizing the function

$$\Phi(n, l)=f_1F_n(\{\rho_i{}^{(1)}\}, T)+f_2F_l(\{\rho_i{}^{(2)}\}, T),$$
$$f_1+f_2=1, \tag{35}$$

where $f_i$ is the volume fraction of the $i$th phase, which should be done for all the sets of the index pairs $n$, $l$ numbering the types of supercrystalline structures, and by selecting phases of such symmetry which should correspond to the absolute minimum of the functional $\Phi(n,l)$ for given values of the parameters and temperature. These results of numerical implementation of the procedure described above are presented in Figs. 1 and 2.

All the phase diagrams shown below are calculated for the following values of the parameters: $m = 10^2$, $N_A = N_B = 10^3$, $v/a^3 = 1$. For example, in Fig. 1a the phase diagram of a weakly charged polyelectrolyte melt is plotted in the $(\chi, \bar{x}_A)$ plane on the assumption that $\varkappa = 1$. The shaded regions are those where two phases coexist simultaneously. The regions are numbered as follows: I) a homogeneous melt liquid (L): II) a region where two homogeneous phases coexist ($L_1$-$L_2$); III) a region where the supercrystalline structure with the lamellar symmetry (l) can be

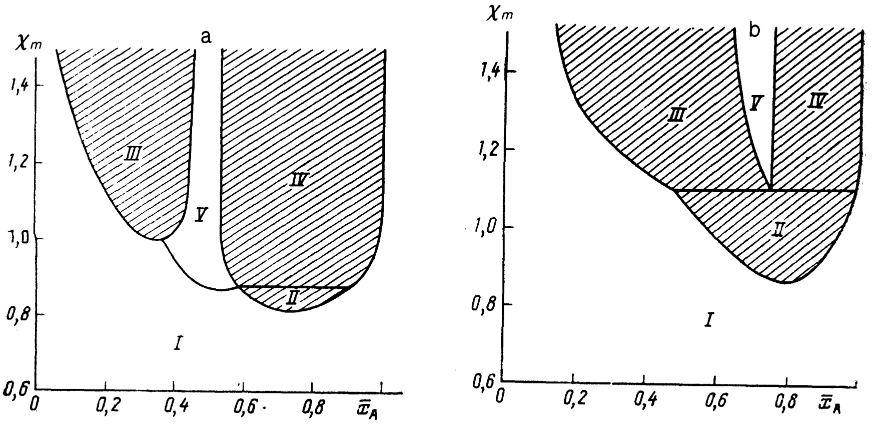


FIG. 1. Phase diagrams of the investigated polymer system calculated in the Brazovskiĭ approximation: a) $\varkappa = 1$; b) $\varkappa = 6$. The shaded regions correspond to the coexistence of two phases. The following regions are identified by numbers: I) L; II) $L_1$-$L_2$; III) $L_1$-$l_1$; IV) $L_2$-$l_2$; V) l.

found; IV), V) regions where the homogeneous and lamellar phases coexist (L–l). The period of the supercrystalline lattice is different in these regions because in our case—in contrast to the case considered by Brazovskiĭ—the pair correlation function depends on the composition of the melt. A characteristic feature of this phase diagram is that when $\tilde{\chi}$ increases (i.e., when temperature is lowered) a "corridor" of composition appears where the melt can exist in the lamellar supercrystalline structure. The change in the behavior of the system as a function of $\varkappa$ is demonstrated in Fig. 1b, where the phase diagram for $\varkappa = 6$ is given. We can see that this new phase diagram still has five regions. However, in contrast to the preceding phase diagram, it has a wide range of regions of the parameter $\tilde{\chi}$ where stratification into two homogeneous phases takes place and the region where the pure lamellar phase exists shifts toward lower temperatures.

Figure 2 gives the phase diagram calculated in the mean-field approximation for $\varkappa = 1$, where the single-phase regions in which a spatially homogeneous melt (L) and supercrystalline structures with symmetries of the body-centered cubic (bcc), triangular ($\Delta$), and lamellar lattices exist are labeled by the numbers I, II, III, and IV, respectively. The regions with compositions corresponding to stratification into two coexisting phases are labeled as follows: V) $\Delta$–$l_1$; VI) bcc–$l_1$; VII) $l_1$–$L_2$; VIII) $l$–$\Delta_2$ and $\Delta_2$–bcc; IX) $L_2$–$l_2$. Comparing the phase diagrams shown in Figs. 1a and 2, we can see that an allowance for the fluctuation effects leads, firstly, to a shift of the transition lines toward lower temperatures (widening of the phase transition region) and, secondly, to suppression of the regions in which phases with higher types of symmetry coexist, i.e., it results in predominance of the phase with the lamellar symmetry, which is typical of weak crystallization.[3,4]

## 5. DISCUSSION OF RESULTS

We have demonstrated that melts of weakly charged polyelectrolytes may exhibit not only supercrystalline phases, but also an equilibrium of these phases with one another and with the spatially homogeneous (liquid) phase. It is natural to ask the question: for which systems and under what conditions can the phase diagrams plotted above be observed? The definitions (25) of the parameters that occur in the conditions (29) for validity of the Brazovskiĭ approximation readily show that in the most interesting region, which is inside the corridor bounding the region of existence of the lamellar phase, both these existence conditions can be readily satisfied for values of $Q_*$ which are not too small, because if $\bar{x}_A = \bar{x}_B = 0.5$, the parameter $\tilde{\gamma}$ vanishes, while the parameter $\tilde{\lambda}$ decreases on increase in $m$ (i.e., on reduction in the degree of ionization of the polyelectrolyte). It therefore follows that the main constraint on the possibility of observing this lamellar phase is the condition

$$Q_*^2 = 1 - s > 0 \quad \text{or} \quad \varkappa = \Theta l_\Theta a^2 / v T_c < 12, \tag{36}$$

where we introduced $l_\Theta = 4\pi e^2/\varepsilon\Theta$ and

$$T_c = \Theta\left\{\frac{l_\Theta a^2}{48v} + \frac{m}{2} + \frac{3vm^2}{l_\Theta a^2}\right\} \tag{37}$$

for the temperature which satisfies the spinodal equation (17a), and in the definition of $s$ we assumed that $\bar{x}_A = \bar{x}_B$. Substituting Eq. (37) into Eq. (36), we can readily show that the latter is equivalent to the inequality

$$l_\Theta a^2 / v < 12m. \tag{38}$$

In the case of what are known as flexible-chain macromolecules, with typical values $a \sim 20$ Å, $v/a^3 \sim 0.1$, and $\Theta \sim 300$–$500$ K, the above inequality is satisfied for $m \gtrsim 4$, which is known to be true in the case of weakly charged polyelectrolytes characterized by $m \gg 1$. However, when the temperature of the system is lowered, the parameter $s$ rises and we first find ourselves outside the range of validity of the Brazovskiĭ approximation, while for $s > 1$ we are also outside the range of existence of supercrystalline phases. Therefore, the theory developed above is valid only in that part of the phase diagram which is shown in the figures.

It also is useful to compare the results obtained in the present study with the phase diagram derived earlier qualitatively by one of the present authors and Boryu[9–11] for a different system in which the coefficient in front of the cubic term does not contain an additional small parameter. In the light of the above analysis we can expect that the structural phase transitions discovered in Refs. 9–11 for such a system in the case of a fixed average composition should be metastable against stratification into two phases of different compositions, but a quantitative analysis of the equilibrium of these phases is outside the framework of the theory of weak crystallization.

We conclude by noting that the mechanism of weak crystallization associated with the presence of a stabilizing Coulomb factor described above is not specific to polymer systems. We can expect similar phase diagrams for other systems of charged particles with long-range correlations of the non-Coulomb origin (such as near-critical electrolytes, systems of charged dislocations, etc.).

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[1)] The phase transition in a system with such a Hamiltonian was first considered by Landau[1] as a special case of the general theory of second-order phase transitions. Considerable progress in the understanding of the fluctuation behavior of systems with this Hamiltonian was made by Brazovskiĭ.[3] We shall therefore refer to it as the Landau–Brazovskiĭ Hamiltonian.

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