Polymer 110 (2017) 49–61

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

# Confinement effects on phase separation of a polyelectrolyte solution

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## ARTICLE INFO

*Article history:*
Received 19 September 2016
Received in revised form
28 November 2016
Accepted 22 December 2016
Available online 29 December 2016

*Keywords:*
Confinement
Self-assembly
Theory

## ABSTRACT

Formulating an analytical theory, we study phase separation of a polyelectrolyte solution under poor solvent condition confined in three types of finite geometric spaces: slab, cylinder, and sphere. Divided by a Lifshitz line, bulk polyelectrolyte solution undergoes either micro- or macro-phase separation. Confinement effects for both scenarios are studied. Composition fluctuations inducing phase separation are classified in terms of eigenmodes of the inverse structure factor operator in the corresponding geometric spaces. Tracking each eigenmode, the instability lines under confinement effects are derived in closed forms. For the confined microphase separation, we find a decaying oscillatory dependence of the spinodal point on the confinement size, which represents the commensurability between the finite period of the soft mode and the confining boundary size. For the confined macrophase separation, a typical mean-field finite size scaling of the Ising universality class is observed under the strong screening condition.

## 1. Introduction

The short-range repulsions between polymer monomers and solvents drive a polyelectrolyte solution under a poor solvent condition to phase separate. However, due to the long-range Coulomb repulsive interaction between polyion charges, domains in a macro-scale cannot be formed. Instead, phase separation proceeds by forming micro-scale domains. In other words, the Coulomb interaction provides a stabilizer for long range composition fluctuations and leads to a microphase separation in a polyelectrolyte-poor solvent system [1]. From this reasoning, it is clear that the system will recover the macrophase separation behavior, which is usual in a polymer solution, once ionic strength is increased to screen the Coulomb interaction to be short-range. These features render a polyelectrolyte solution to be a fascinating system of studying phase separation behaviors.

Theoretical studies of phase separation in a polyelectrolyte solution have been carried out during past decades [2–8]. Borue and Erukhimovich formulated a microscopic statistical theory for the weakly charged polyelectrolyte solution within the framework of the random phase approximation (RPA) [3]. Through analyzing the correlation functions, a microphase separation was reported in their paper. Later, this work has been developed in terms of the weak crystallization theory and phase diagrams have been constructed for this system [4,5]. The correlation functions of different components have been derived and analyzed carefully [6–8]. On the experimental side, the microphase separation of a polyelectrolyte solution has also been observed by several groups [9–11].

Obtaining ordered structures through the microphase separation of block copolymer system has been an active research area in polymer community for decades [12–14]. Besides the classic morphologies formed in a bulk block copolymer system, it has been established that confinements generate significant effects on phase behavior of block copolymer self-assembly; novel structures, which are absent in a bulk system, can be created by confining bulk system into finite geometric spaces. As the result, nanolithography, which is to utilize confinement effects for self assembling, has become a promising and fast developing research area in recent years [15]. Compared to this situation, the microphase separation of a polyelectrolyte solution, which provides a new possible route to create nanostructures, has not been widely noticed and systematically investigated up to now. In particular, how does confinement affect phase separation of a polyelectrolyte solution? What types of novel morphologies can be induced through introducing confinements into a polyelectrolyte solution? These remain to be important yet unanswered questions. In addition to the importance from the viewpoint of nanolithography, clarifying these questions about

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http://dx.doi.org/10.1016/j.polymer.2016.12.061

polyelectrolyte phase behaviors within confined spaces will shed lights on the understanding of bio-systems, considering that biomacromolecules, which are essentially polyelectrolytes, are under a confined environment within a cell. Furthermore, the confinement effect on phase transition has been a fascinating research topic in statistical mechanics [16–25]. Studies have shown that the critical temperature is shifted relative to the bulk value adopting a scaling form in the confined binary small molecule and polymer thin films [18–20]. Due to the fact that two types of transitions, micro- and macro-phase separation, can occur in one model of a polyelectrolyte solution by adjusting screening strength, studying the confined polyelectrolyte solution can provide important insights for the fundamental research of phase transitions in confined spaces.

Motivated by these factors, we address phase separation of a polyelectrolyte solution within confined spaces theoretically in this manuscript. To our knowledge, this work is the first theoretical investigation towards the understanding of confinement effects on self-assembly in a polyelectrolyte solution. Specifically, we formulate an analytical model, which originates from our theoretical methods developed for studying the block copolymer melts within confined spaces [26,27]. This calculational framework has also been developed by Erukhimovich et al. independently [28,29]. Three types of confinement scenarios have been invoked in this paper. Namely, the polyelectrolyte solution is confined between two infinite parallel plates (slab), within an infinitely long cylindrical pore (cylinder), and within a spherical pore (sphere), respectively. As the main results, the instability lines are derived in closed forms by tracking eigenmodes of fluctuations. For the slab and the cylinder confinements, on one hand, the spinodal point experiences no difference from the bulk correspondence, which is attributed to the existence of free dimensions in these two set-ups of confinements, wherefrom the perpendicular mode free of confinements induces the instability of the homogeneous phase; on the other hand, through analyzing eigenmodes, a degenerate soft-mode set is identified for the confined microphase separation which, due to the competition among the degenerate modes, leads to complex morphologies in the confined space. For the sphere confinement, the spinodal of the microphase separation behaves a decaying oscillatory dependence on the confining size. This represents the commensurability between the finite size of the spherical pore and the natural period of the soft mode. A re-entrance of the disordered phase is observed in the phase diagram with increasing the pore size around the bulk spinodal temperature. On the macrophase separation side, confinement leads the instability point shift, relative to the bulk value, to behave a typical mean-field finite size scaling of the Ising universality class under the strong screening condition.

The paper is organized as follows. In Section 2, we derive the correlation matrix for the polyelectrolyte system through a general way. Section 3 introduces confinements into the system, fluctuation modes are classified in terms of eigenmodes, instability lines are derived. In Section 4, we discuss the results. Section 5 gives a conclusion.

## 2. Phase separation in bulk

Consider a polyelectrolyte solution. There are four types of components in the system: polyions, counterions, salts, and solvents. Polyions are weakly charged and treated as flexible polymer chains with a homogeneous charge distribution along each chain contour; for each polyion chain, the degree of polymerization is $N$, the Kuhn length is $b$, the fraction of charged monomers with charge $-e$ is $f$, the excluded volume parameter of monomers is $\upsilon$, and the third virial coefficient is $\omega$, which is a positive constant. Here $e$ denotes the elementary charge unit. Monovalent counterions and salts move around in the system volume $V$. The average densities of polymer monomers, counterions, and salts are $\phi_0, \phi_{c,0}$, and $n_0$, respectively. The global electroneutrality of the system enforces the constraint of $f\phi_0 + n_0 = \phi_{c,0}$. Note that counterions include positively charged ions dissociated from both polyions and salts. Solvents are treated in an implicit way by introducing a homogeneous background dielectric constant $\varepsilon$. In the calculation, all the lengths are scaled to be dimensionless by the Kuhn length $b$.

To study the phase separation of a homogeneous polyelectrolyte solution, we formulate a Gaussian fluctuation theory here. Start with the homogenous phase, we define a vector field, $\overrightarrow{\phi}(\mathbf{r}) = \{\phi(\mathbf{r}), \phi_c(\mathbf{r}), n(\mathbf{r})\}$, to characterize the density fluctuations from the homogeneous state for polymer monomers, counterions, and salts, respectively. In the Gaussian level, this order parameter is subject to a Hamiltonian

$$\beta H = \frac{1}{2V}\sum_{\mathbf{q}} \overrightarrow{\phi}(\mathbf{q})\mathbf{S}^{-1}(\mathbf{q})\overrightarrow{\phi}(-\mathbf{q})^T \tag{1}$$

which has been written down in the reciprocal space to utilize the translational invariance of the homogenous solution. Here $\beta = 1/k_BT$ with $k_B$ being the Boltzmann constant and $T$ being the absolute temperature; $\overrightarrow{\phi}(\mathbf{q})$ stands for the Fourier transform of $\overrightarrow{\phi}(\mathbf{r})$; the coefficient matrix $\mathbf{S}^{-1}(\mathbf{q})$ captures the energy spectrum of fluctuation modes labelled by the wave vector $\mathbf{q}$.

In the Gaussian fluctuation theory, the coefficient matrix is constructed as $\mathbf{S}^{-1}(\mathbf{q}) = \mathbf{S}_0^{-1}(\mathbf{q}) + \mathbf{V}_0(\mathbf{q})$, where $\mathbf{S}_0^{-1}(\mathbf{q})$ and $\mathbf{V}_0(\mathbf{q})$ stand for the inverse bare correlation matrix and the bare interaction matrix, respectively [30,31]. As exposed in detail in the Appendix, substituting related quantities, we have

$$\mathbf{S}^{-1}(\mathbf{q}) = \begin{pmatrix} S_0^{-1}(\mathbf{q}) + \upsilon + \omega\phi_0 + 4\pi l_B f^2\big/q^2 & -4\pi l_B f\big/q^2 & 4\pi l_B f\big/q^2 \\ -4\pi l_B f\big/q^2 & \phi_{0,c}^{-1} + 4\pi l_B\big/q^2 & -4\pi l_B\big/q^2 \\ 4\pi l_B f\big/q^2 & -4\pi l_B\big/q^2 & n_0^{-1} + 4\pi l_B\big/q^2 \end{pmatrix} \tag{2}$$

where $S_0(\mathbf{q})$ is the structure factor of the polyion in the reference interaction-free system, which is taken to be the approximate Debye function, $S_0(\mathbf{q}) = S_0(q) = (N\phi_0)/[1 + q^2R_g^2/2]$ with $R_g^2 = N/6$ being the mean-square radius of gyration for an ideal chain. Note that, by choosing this form, we are dealing with flexible chains for the weakly charged polyelectrolytes. $l_B = e^2/(4\pi\varepsilon k_BT)$ is the Bjerrum length characterizing the strength of the electrostatic interaction. $\upsilon = 1 - 2\chi$ is the excluded volume parameter between the polyelectrolyte monomers with $\chi$ being the Flory-Huggins parameter dependent on the temperature.