CAPILLARY-INDUCED SELF-COACERVATION IN ZWITTERIONIC POLYMER SOLUTIONS: A MEAN-FIELD THEORY

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We investigate the phase behavior of zwitterionic polymer solutions confined within attractive slit-like nanopores. Extending a previous mean-field model for bulk self-coacervation [1], we incorporate chain connectivity, excluded volume, electrostatic dipole-dipole correlations, and adsorbing pore walls. Using a thermomechanical approach based on Noether's theorem [2], we compute disjoining pressure, which characterize the underlying phase behavior.

The results show that strong electrostatic correlations, combined with preferential wall adsorption, can induce capillary-driven liquid-liquid phase separation within the pore — a "capillary-induced self-coacervation". This leads to the formation of a dense coacervate film bridging the opposing walls, which subsequently ruptures upon increasing pore width, producing highly non-monotonic disjoining pressure curves.

A key finding is the crossover between two distinct film formation mechanisms depending on the strength of polymer-wall attraction. In the weak adsorption regime, bridging by single chains dominates, with the critical pore width scaling as $H_c \sim N^{1/2}$, reflecting the chain size. In the strong adsorption regime, the system enters a cohesion-dominated regime, where the critical pore width saturates to an N-independent plateau, indicating that film formation is driven by a confinement-induced shift of the local binodal that stabilizes a cohesive coacervate phase even when the bulk is supercritical.

1. Budkov Y. A., Brandyshev P. E., Kalikin N. N. Theory of self-coacervation in semi-dilute and concentrated zwitterionic polymer solutions // Soft Matter. – 2023. – V. 19. – N. 18. – P. 3281-3289.

2. Budkov Y. A., Kalikin N. N., Brandyshev P. E. Thermomechanical approach to calculating mechanical stresses in inhomogeneous fluids and its applications to ionic fluids // Journal of Statistical Mechanics: Theory and Experiment. – 2024. – N. 12. – Article 123201.

This work was carried out with support of the RSF (grant 24-11-00096).