Phase transition in hydrophobic PE gels

Alexander D. Kazakov, Varvara M. Prokacheva, Oleg V. Rud, Lucia Nová and Filip Uhlík

Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University, Hlavova 8, 128 00 Praha 2, Czech Republic.

Abstract

We present simulations and analytical theory of phase transition of polyelectrolyte hydrophobic gel. We provide the dependency of applied pressure as a function of gel density φ as well as its ionization degree α. Additionally, we provide the state diagram of hydrophobic gel with respect to simulations as well as analytical theory based on box model. Finally we ...

Keywords: hydrophobic gel; box-model; Langevin dynamics; desalination

Compile date: May 10, 2022

Todo list

(VP.27.4) Do we need to add these plots as our expectation from MD based?If yes, I'll improve pictures, If not then I'll just delete them 4

1. Analytical theory

In order to obtain analytical results of hydrogel compression we use the mean-field approximation based on the classical lattice Flory theory of polymer. In such an approximation, hydrogel is represented by the network of PE chains connected by thetrafunctional crosslinks. Because all chains are considered to be uniformly and equally stretched this approximation is also called the box-like model. An end-to-end distance of one chain R is defined by its length N and the average polymer concentration φ as well as geometry of the network

$$R = \left(\frac{AN}{\varphi}\right)^{1/3} \tag{1}$$

We consider a diamond-like structure of the gel that corresponds to $A = 3\sqrt{3}/4$.

The free energy of a single chain of the gel consists of three independent terms

$$F(\varphi) = F_{\mathrm{conf}}(\varphi) + F_{\mathrm{int}}(\varphi) + F_{\mathrm{ion}}(\varphi) \tag{2}$$

We express all the energies in $k_{\mathrm{B}}T$ units and all lengths in the monomer unit length σ.

The first term in Eq. 2 corresponds to the conformational free energy of an uniformly and finitely extended chain [1].

$$F_{\mathrm{conf}} = \frac{3}{2}\left[\frac{R^2/(Nb^2) - 1}{(1 - R^2/(N^2b^2))^d} - \ln\left(\frac{R^2}{Nb^2}\right)\right], \tag{3}$$

where the first term includes Gaussian elasticity and the logarithmic term accounts for the effect of chain compression, d is a non-negative parameter characterizing the divergence behaviour of the stretching energy.

*Corresponding author