Follow substitution of Eq. 9, Eq. 10 and Eq. 11 into Eq. 8 gives as finall equation for the pressure with only unknown parameter α. That can be found as a solution of separated polynomial equation for certain c_s, $\alpha_\mathrm{b} = \dfrac{1}{1+10^{-(\mathrm{pH}-\mathrm{p}K)}}$ and φ

$$-\alpha_\mathrm{b}\left(1-\alpha_\mathrm{b}\right)\alpha^3 + \left[\frac{c_\mathrm{s}}{\varphi}\left(1-2\alpha_\mathrm{b}\right) + \alpha_\mathrm{b}\left(1-\alpha_\mathrm{b}\right)\right]\alpha^2 + \frac{2c_\mathrm{s}\alpha_\mathrm{b}^2}{\varphi}\alpha - \frac{c_\mathrm{s}\alpha_\mathrm{b}^2}{\varphi} = 0 \tag{12}$$

2. Results and Discussion

2.1. Pressure extension curve

A decrease in the salt concentration, $\mathrm{pH}-\mathrm{p}K$ difference and/or deterioration of solvent quality leads to the phase separation in gels. The presence of such separation affects the hydrogel pressure-extension curve that appears to be non-monotonic dependence having a loop form. One of the possible ways to obtain an experimentally observable pressure-extension curve is to build the Maxwell construction. The final result of that can be found in the main file of the publication. Here we present original pressure-extension curves obtained from simulations in one plot Fig. 1 as well as compare (in left and right column) different $\mathrm{pH}-\mathrm{p}K$, namely, $\mathrm{p}K = 5$ and $\mathrm{p}K = 6$, respectively. The less $\mathrm{pH}-\mathrm{p}K$ is, the wider range of ε and/or c_s at which the phase separation takes place becomes. We mark the points of the two phases' coexistence with white triangles and the points of local maximum and minimum pressure with orange triangles. The connection of all white triangles gives the U-shaped coexistence curve (binodal), while the connection of orange triangles gives a curve (spinodal) that separates the region of metastable states from the region of unstable states.

2.1.1. Maxwell construction procedure

In Fig. 2 we show the picture of the Maxwell construction. For different $\mathrm{p}K$ values as well as salt concentrations c_s, we build Maxwell construction in order to find transition pressure. Additionally, we depict the left and right boundaries of the construction as well as local minimum and local maximum. Taking into account these highlighted volumes it is possible to find out phase coexistence region.

We implemented a Maxwell construction procedure in a small python script. The idea is to find horizontal line drawn so that it cuts loops of equal areas above and below the line. The pressure corresponded to this line is a transition pressure. The code and details of the procedure are available on GitHub.

2.2. Ionization degree

For the same systems, we plot the change of hydrogel ionization degree upon compression Fig. 3.

2.3. Phase diagram

In order to compare results of MD simulations with results of the box-model we need to understand the relation between χ and ε parameters defined the solvent quality in each model. To do that we fit MD data with the analytical equation of the box-model Eq. 7.

2.3.1. Fitting

In Fig. 4 we show fit of MD data using analytical equation. The fits were performed with bootstrap routine involved. Initially, we increased number of data points interpolating of MD data. By this procedure we only increased number of points in the region of high gel dense where the pressure sharply increases to high values with compression. Additionally, we decreased the number of points at low density. By doing this we would like to create a small "educational" bias for the fitting procedure. Simultaneously, we increased the error bar estimation by 30% of the value in order to make the fit flexible enough to put into consideration "good enough" realizations too.

We performed 1k random deletions of 95% data points per curve. On each realization we performed fit procedure using Trust Region Reflective (TRF) method. We allowed changes in χ value from 0.0 to 5.0, number of segments per chain was almost fixed to number of segments in MD simulation with small deviation to ± 1. Additionally, we allowed to vary hyperparameter d in range of 0.5 to 1.5, as well as size of monomer σ in range of 0.34 to 0.36 nm.