

Phase transition in hydrophobic PE gels

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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

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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

5 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 tetrafunctional 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.

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

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

$$F(\varphi) = F_{\text{conf}}(\varphi) + F_{\text{int}}(\varphi) + F_{\text{ion}}(\varphi) \quad (2)$$

We express all the energies in $k_B T$ 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].

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

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.

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The second term in Eq. 2 is the contribution of non-electrostatic (excluded volume) interactions accounted for the mobile ions volume as well

$$F_{\text{int}} = \frac{N}{\varphi} [(1 - \varphi - \varphi_+ - \varphi_-) \ln(1 - \varphi - \varphi_+ - \varphi_-) + \chi \varphi (1 - \varphi - \varphi_+ - \varphi_-)], \quad (4)$$

- where the first term is the entropy of solvent molecules and the second is the energy of volume interactions defined by the Flory-Huggins parameter χ . The value $\chi = 0$ corresponds to athermal solvent, $\chi = 0.5$ – the theta-solvent and $\chi > 0.5$ corresponds to a poor solvent.

The third term in Eq. 2 accounts for ionic contributions: the translational entropy of mobile ions and for their partial pressure inside and outside the gel

$$F_{\text{ion}} = \frac{2c_s N}{\varphi} \left[1 - \sqrt{1 + \left(\frac{\alpha \varphi}{2c_s} \right)^2} \right] + N \ln(1 - \alpha) \quad (5)$$

where ionization degree, α , is calculated based on local ionization equilibrium and the local electroneutrality condition from the following equation

$$\frac{\alpha}{1 - \alpha} 10^{PK - pH} = \sqrt{1 + \left(\frac{\alpha \varphi}{2c_s} \right)^2} - \frac{\alpha \varphi}{2c_s} \quad (6)$$

The derivation of the last two equations can be found in [2, 3].

Thus, taking a derivative of the hydrogel free energy Eq. 2 with respect to the gel volume, one could obtain the hydrogel partial pressure p or other words, the pressure needed to be applied to the hydrogel using a semipermeable sieve in order to make gel density equal to φ

$$p(\varphi, c_s) = - \left(\frac{\partial F(\varphi(V_{\text{gel}}), c_s)}{\partial V_{\text{gel}}} \right)_{c_s} \quad (7)$$

Because we assume all term of free energy independent we can work on them separately as following

$$p(\varphi, c_s) = - \left(\frac{dF_{\text{conf}}}{dV} + \frac{dF_{\text{int}}}{dV} + \frac{dF_{\text{ion}}}{dV} \right) \quad (8)$$

$$\frac{dF_{\text{conf}}}{dV} = \frac{A^{2/3} N^{d-1} \left(1 - d \frac{1 - (AN/\varphi)^{2/3}}{N - (AN/\varphi)^{2/3}} \right)}{(N/\varphi)^{1/3} (N - (AN/\varphi)^{2/3})^d} - \frac{\varphi}{N} \quad (9)$$

$$\frac{dF_{\text{int}}}{dV} = \left(1 - \frac{c_s}{\xi} - c_s \xi \right) \ln \left(1 - \varphi - \frac{c_s}{\xi} - c_s \xi \right) + \varphi + \chi \varphi^2 + \frac{\left(\frac{c_s}{\xi} - c_s \xi \right) \left[\ln \left(1 - \varphi - \frac{c_s}{\xi} - c_s \xi \right) + \varphi + \chi \varphi^2 \right]}{(2 - \alpha) \alpha \varphi + \frac{2c_s \xi}{\alpha}}, \quad (10)$$

$$\text{where } \xi = \frac{\alpha (1 - \alpha_b)}{\alpha_b (1 - \alpha)} = \sqrt{1 + \left(\frac{\alpha \varphi}{2c_s} \right)^2} - \frac{\alpha \varphi}{2c_s}$$

$$\frac{dF_{\text{ion}}}{dV} = -2c_s \left(\sqrt{1 + \left(\frac{\alpha \varphi}{2c_s} \right)^2} - 1 \right) \quad (11)$$

Follow substitution of Eq. 9, Eq. 10 and Eq. 11 into Eq. 8 gives as final equation for the pressure with only unknown parameter α . That can be found as a solution of separated polynomial equation for certain

$$c_s, \alpha_b = \frac{1}{1 + 10^{-(pH - pK)}} \text{ and } \varphi$$

$$-\alpha_b(1 - \alpha_b)\alpha^3 + \left[\frac{c_s}{\varphi}(1 - 2\alpha_b) + \alpha_b(1 - \alpha_b) \right] \alpha^2 + \frac{2c_s\alpha_b^2}{\varphi} \alpha - \frac{c_s\alpha_b^2}{\varphi} = 0 \quad (12)$$

15 2. Results and Discussion

2.1. Pressure extension curve

A decrease in the salt concentration, $pH - pK$ 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 $pH - pK$, namely, $pK = 5$ and $pK = 6$, respectively. The less $pH - pK$ 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 pK 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.

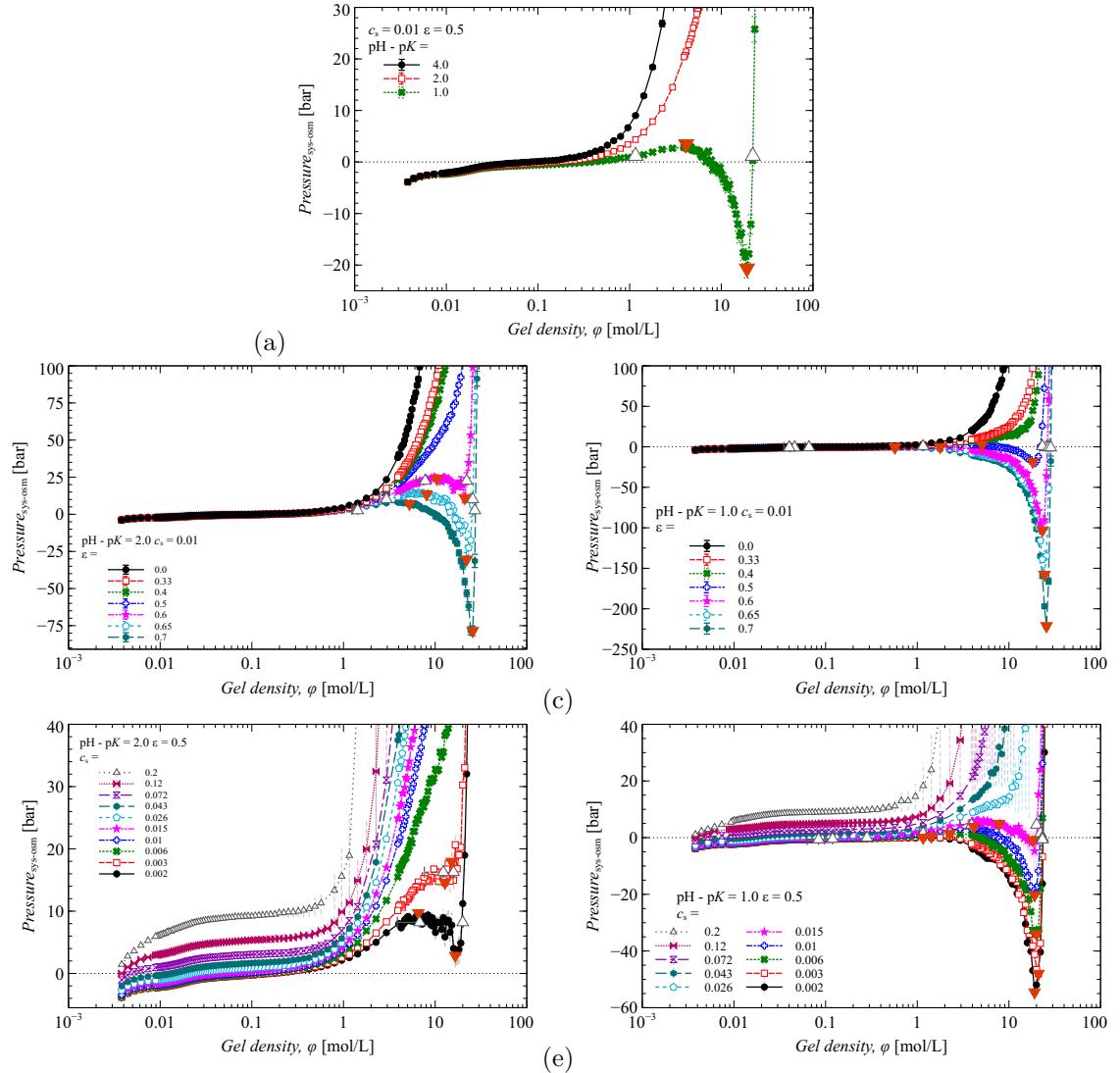


Figure 1: Dependence of the pressure P applied to the gel in order to compress it to a certain density as a function of this gel density φ for different (a) ionization constant pK of the gel, (b)-(c) solvent quality and (d)-(e) salt concentration c_s .

55 2.3.2. Box-model predictions

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Eq. 7 can provide us a set of pressure-extension curves varying, *e.g.* salt concentration. Afterwards we can convert this set into a phase diagram, *e.g.* in coordinates of salt concentration - gel density as shown in Fig. 5. In Fig. 5(a) we plot several phase diagram for different solvent quality at constant $pH - pK = 2$, while in Fig. 5(b) we show how $pH - pK$ difference change the phase diagram. Each of them has a U-shaped curvature. Firstly, an increase of $pH - pK$ difference that can be considered as an increase of pH or moving to more charged PE gel leads to the presence of hydrogel in two phases states at lower salinity. Secondly, a deterioration of the solvent quality (increase χ) results in a shift of the curves to high salt concentrations, thereby increases the region of two phases states of the hydrogel. Thus, we expected from simulations similar results.

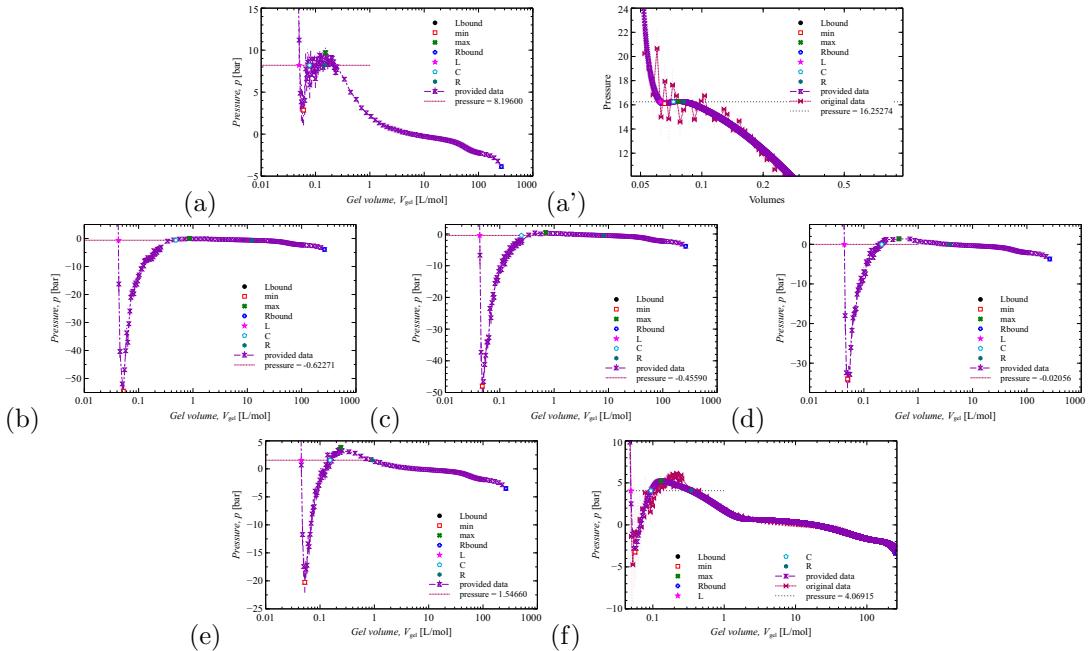


Figure 2: Results of the Maxwell constructions on pressure-extension curves of gels with the same hydrophobicity $\varepsilon = 0.5$ and at different salt concentration: (a) $pK = 5.0$, $c_s = 0.002$, (a') $c_s = 0.003$, the rest is for $pK = 6.0$ and (b) $c_s = 0.002$, (c) $c_s = 0.003$, (d) $c_s = 0.006$, (e) $c_s = 0.01$, (f) $c_s = 0.015$. Approximate value of the transition pressure is written in the legend and represented by the dashed horizontal line.

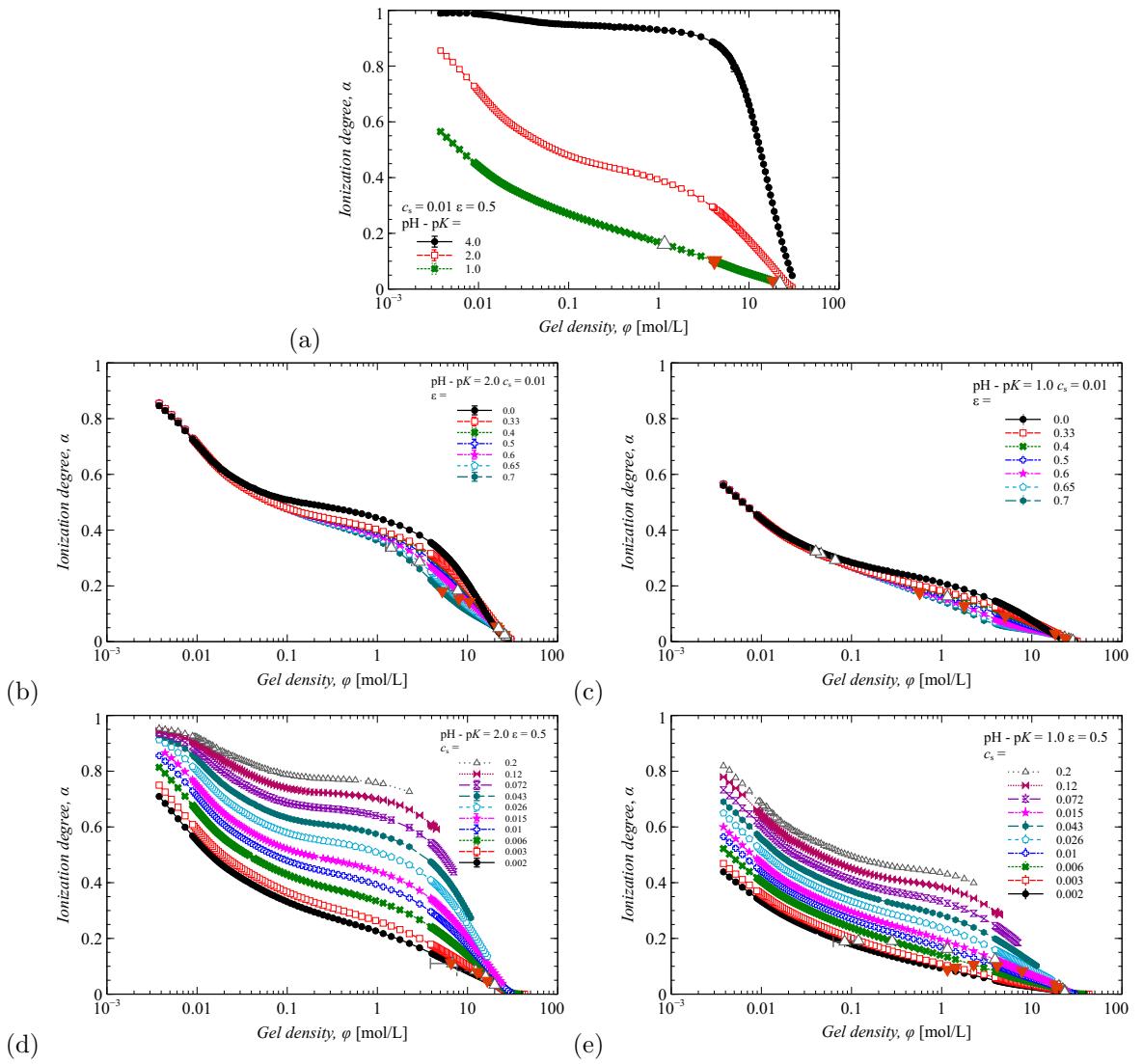


Figure 3: Ionization degree α of the gel as a function of gel density φ for different (a) ionization constant pK of the gel, (b)-(c) solvent quality and (d)-(e) salt concentration c_s .

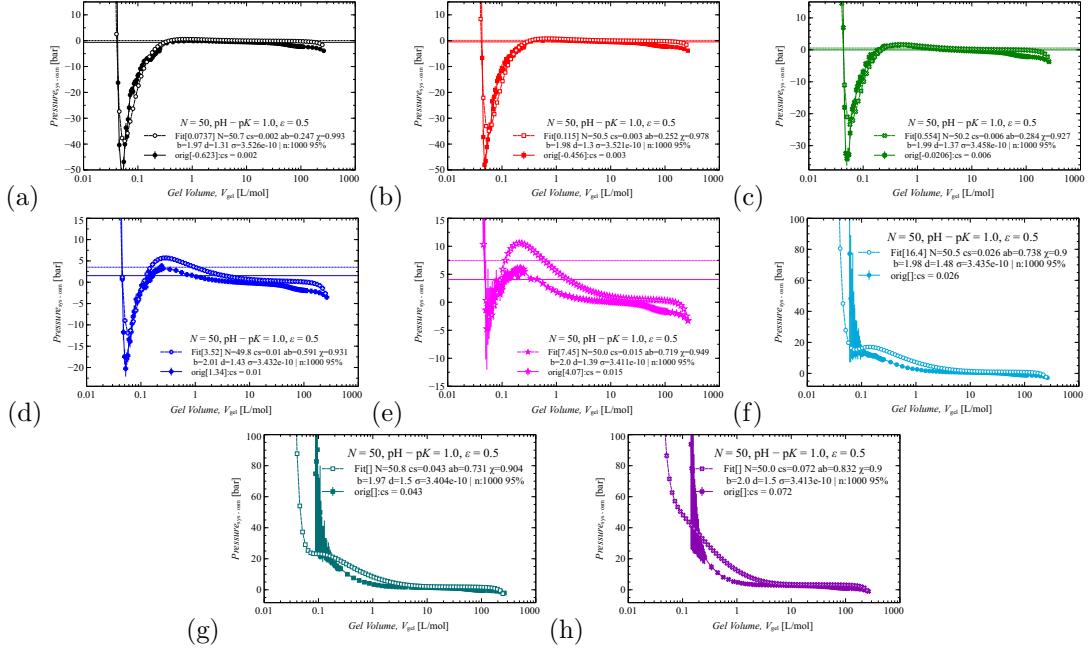


Figure 4: Results of the bootstrap fit of pressure-extension curves of gels with $pK = 6.0$ and the same hydrophobicity $\varepsilon = 0.5$ and at different salt concentration: (a) $c_s = 0.002$, (b) $c_s = 0.003$, (c) $c_s = 0.006$, (d) $c_s = 0.01$, (e) $c_s = 0.015$, (f) $c_s = 0.026$, (g) $c_s = 0.043$, (h) $c_s = 0.072$. The result of the fitting is an approximate value of χ parameter written in the legend.

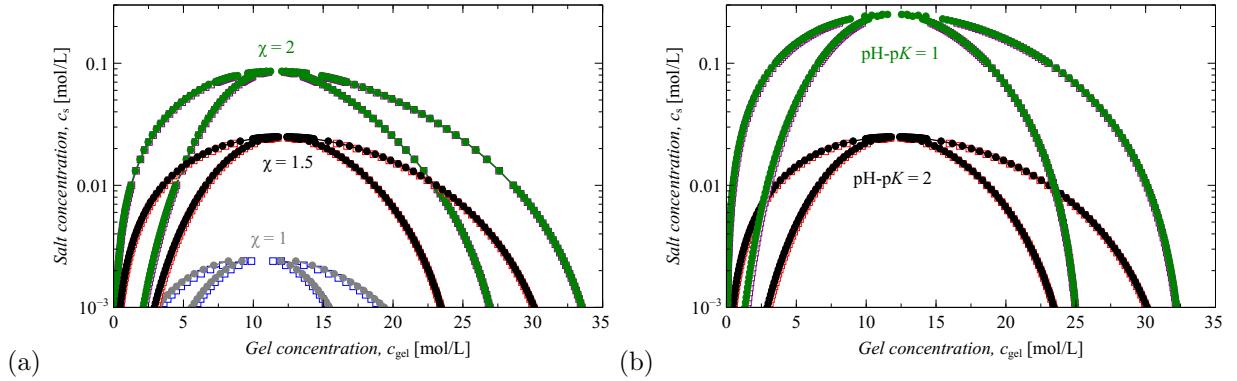


Figure 5: Phase diagrams of hydrophobic gel in salt concentration c_s – gel concentration coordinates obtained from the box-model (a) at constant $pH - pK = 2$ and different solvent quality χ , (b) at constant solvent quality $\chi = 1.5$ and different $pH - pK$. Blue, red and dark-magenta colors correspond to $b = 2$, while grey, black and green – $b = 1$.

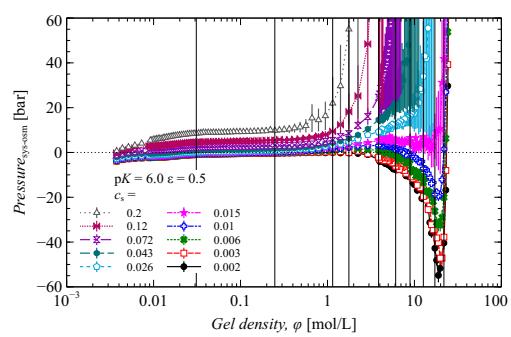


Figure 6: Pressure - extension curve of hydrophobic gel $pH - pK = 1$, $\varepsilon = 0.5$ at different salt concentration c_s .

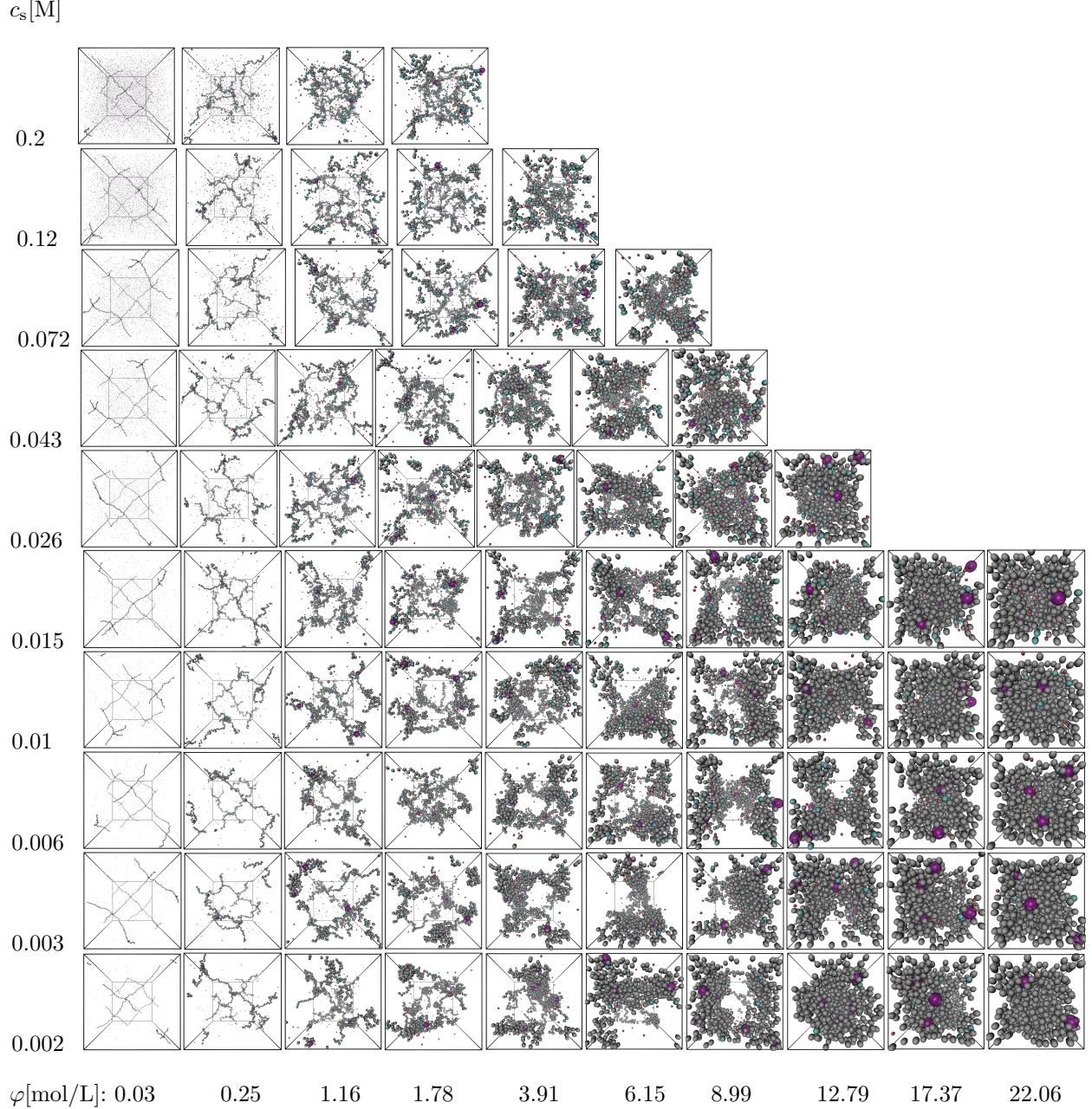


Figure 7: Snapshots of hydrophobic gel with $\text{pH} - \text{p}K = 1, \varepsilon = 0.5$ correspond to the systems from at densities marked by vertical lines. Each row corresponds to a certain salt concentration c_s and each column – gel density. Approximate values of the gel density φ corresponded to the region of the phase transition are calculated after the Maxwell construction (see Fig. 2): [0.07 – 23.26] at $c_s = 0.002$, [0.09 – 23.26] at $c_s = 0.003$, [0.14–22.73] at $c_s = 0.006$, [1.25–22.22] at $c_s = 0.01$, [3.85–14.71] at $c_s = 0.015$.

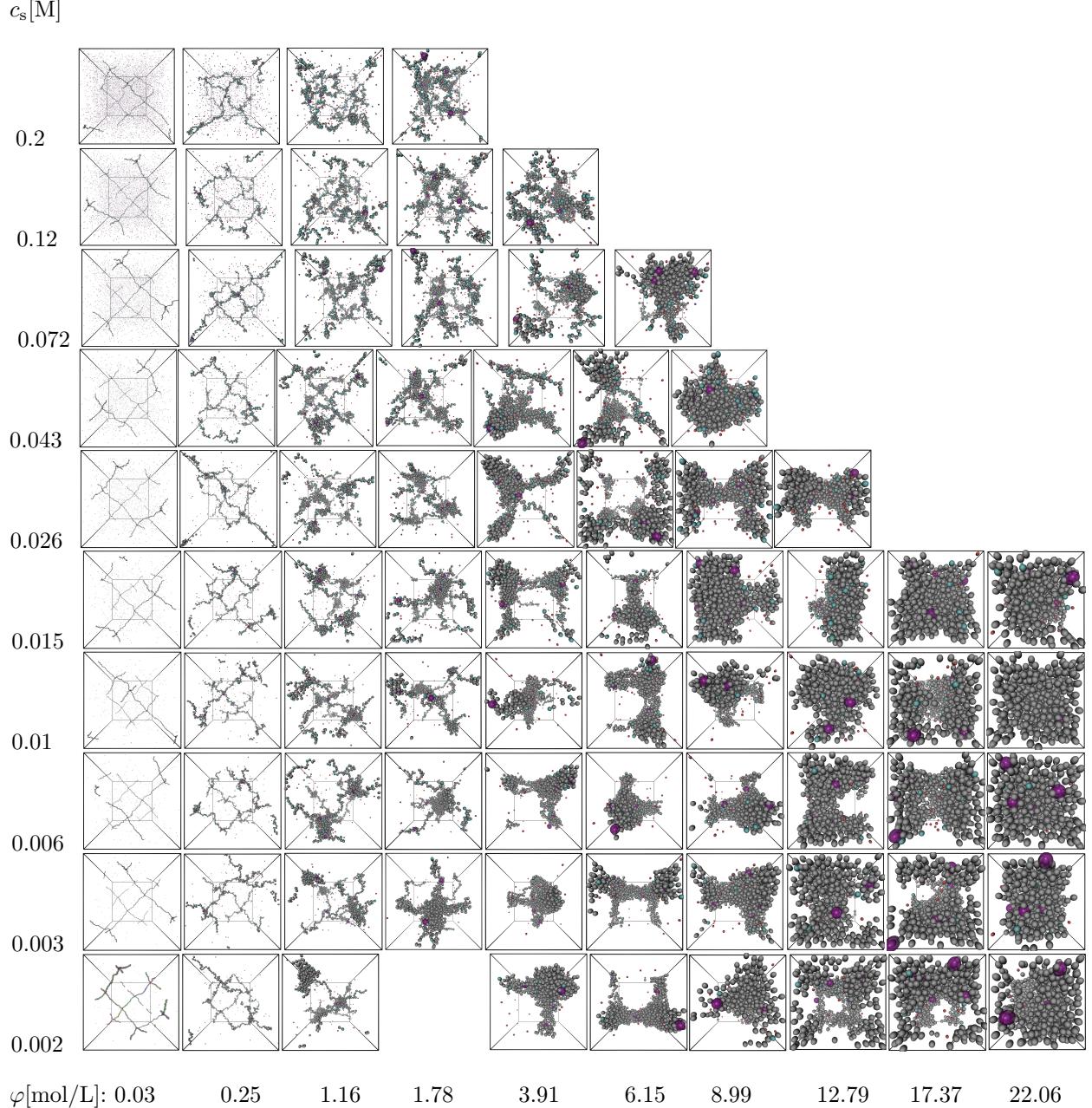


Figure 8: Snapshots of hydrophobic gel with $\text{pH} - \text{p}K = 1, \varepsilon = 0.7$ correspond to the systems from at densities marked by vertical lines. Each row corresponds to a certain salt concentration c_s and each column – gel density. Approximate values of the gel density φ corresponded to the region of the phase transition are calculated after the Maxwell construction (see Fig. 2): [0.07–23.26] at $c_s = 0.002$, [0.09–23.26] at $c_s = 0.003$, [0.14–22.73] at $c_s = 0.006$, [1.25–22.22] at $c_s = 0.01$, [3.85–14.71] at $c_s = 0.015$.

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