Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Poly(sodium acrylate) hydrogels: Synthesis of various network architectures, local molecular dynamics, salt partitioning, desalination and simulation

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1 Mapping of initial salt concentrations between Experiments and the Simulations

In the experiments we use a salt solution of given (initial) salt concentration c_0 in a chamber of volume V. Dry polymeric gel is added until the gel volume V_{gel} and the volume of the supernatant salt solution $V_{\text{supernatant}}$ are half the volume of the chamber $V_{\text{gel}} = V_{\text{supernatant}} = V/2$. The number of salt ion pairs in the volume is given by $N_{\text{s}} = c_0 V$ which needs to be conserved in the whole process. Therefore, the number of salt ion pairs in the supernatant phase $N_{\text{s,supernatant}}$ and the number of salt ion pairs in the gel phase $N_{\text{s,gel}}$ sum up to the total number of ion pairs $N_{\text{s}} = N_{\text{s,gel}} + N_{\text{s,supernatant}}$. The numbers in the respective gel or supernatant phase can again be calculated from the respective salt concentrations $(c_{\text{in}}, c_{\text{out}})$ and volumes of these phases: $N_{\text{s,gel}} = c_{\text{in}} V_{\text{gel}} = c_{\text{in}} V/2$ and $N_{\text{s,supernatant}} = c_{\text{out}} V_{\text{supernatant}} = c_{\text{out}} V/2$. Plugging these particle numbers in the equation for the particle number conservation gives:

$$N_s = c_0 V = \frac{c_{\mathrm{in}} V}{2} + \frac{c_{\mathrm{out}} V}{2}, \tag{1}$$

which can be rearranged:

$$c_0 = \frac{c_{\mathrm{in}} + c_{\mathrm{out}}}{2}. \tag{2}$$

We use the formula above for calculating the initial salt concentration c_0 based on c_{in} and c_{out}.

2 Parameters

Since we simulated poly(acrylic acid) in contact with a solution at pH=7 we choose the gel monomers to be fully charged ($f = 1$) and carry a negative charge in our simulations. At pH=7 the H^+ and OH^- concentrations are very low and therefore we neglect them in our simulations. In the PB model we perform simulations with different choices of the chain length $N \in \{15, 20, 30, 50\}$ as indicated in the main paper (see Fig. 6). The interpenetrating gel simulations were carried for a chain length of $N = 40$ and various salt concentrations in the supernatant phase $c_{\mathrm{out}} \in \{0.01, 0.02, 0.05, 0.1, 0.2\}$ mol/L. The resulting initial salt concentrations c_0 for Fig. 7 were calculated as indicated above using the resulting salt concentrations inside the gel c_{in}.

3 Poisson Boltzmann Simulations

For details of the model we refer to previous publications where we introduced the Poisson-Boltzmann cell gel model.[5,6] The core idea of the model is to describe the behavior of a single chain instead of a network of chains. If a gel is compressed the end-to-end distance of the chains and the volume which is available to the chain is reduced. We therefore assign a cylindrical volume $V_{\mathrm{chain}}(R_{\mathrm{e}}) = R_{\mathrm{e}}^3/A$ to the chain which depends on its end-to-end distance and where $A = \sqrt{27}/4 \approx 1.3$. The value for A arises from simple geometrical considerations for a fully stretched diamond-like network.[4,6] In order to mimic the electrostatic environment in the gel, where one end of the chain sees the beginning of the next chain we periodically replicate the cylinder in the axial direction. Therefore, we effectively deal with the electrostatic problem of an infinite, penetrable, charged rod. The volume V_{chain} of the gel is in total electroneutral. The single chain is described as fixed charge density $\rho_f(\vec{r})$ and elastic contributions.[5,6] The charge density of the ion species i is $\rho_i(\vec{r}) = c_i(\vec{r})q_i$ and is given by the particle number density $c_i(\vec{r})$ and the charge of the ions q_i. The densities of the ion species are distributed according to

$$c_i(r) = c_{\text{i,supernatant}} e^{\frac{-q_{\pm}\psi(x,y,z)}{k_{\text{B}}T}}, \tag{3}$$

where $c_{\text{i,supernatant}} = c_{\text{out}}$ are the ion densities in the reservoir and where $k_{\text{B}}T$ is the absolute temperature times the Boltzmann constant. The total electric potential ψ is obtained via a finite element solver solving the Poisson-Boltzmann equation:

$$\nabla^2\psi = -\frac{1}{\varepsilon_r\epsilon_0}\left(\sum_i q_i c_i(\vec{r}) + \rho_f(\vec{r})\right), \tag{4}$$

where ε_r is the relative permittivity, which we choose to be 80 (to mimic water).

Knowing the ion distributions, the electrostatic potential and the elastic contributions of the model[5,6] we can evaluate the pressure of the system. The pressure in the gel is calculated using the electrostatic Maxwell pressure, the kinetic pressure and a stretching pressure.[5,6] For further details on how to calculate the pressure in the gel $P_{\text{in}}(V)$ we refer to previous publications.[5,6] Performing multiple simulations at different volumes gives pressure volume curves which allow to find the swelling equilibrium of the gel:

$$P_{\text{in}}(V_{\text{eq}}) = P_{\text{supernatant}}. \tag{5}$$

The reservoir pressure is approximated by the ideal gas pressure of the ions in the supernatant solution. Information about the salt partitioning can be obtained via comparing the average ion concentration in the volume which is available to the chain $c_{\text{in}} = \langle c_- \rangle_V = \frac{1}{V}\int_V dV c_-(\vec{r})$ to the ion concentration in the supernatant phase c_{out}. Since the counter ions of the negatively charged gel are positive, the concentration of negative monovalent ions is chosen to determine the salt concentration inside the gel.

4 Molecular Dynamics Simulations

The molecular dynamics (MD) simulations are carried out with the simulation package ESPResSo.[8] In order to simulate an interpenetrating network of two gels we first setup a single diamond like gel. Then we create the second interpenetrating network via creating a new gel with coordinates exactly shifted by half of the box length in each Cartesian direction. The interpenetrating networks then are similar to the ones used by Edgecombe *et al.*[2] We employ the Langevin thermostat to set the temperature in the simulation. The Langevin equation is integrated using a velocity Verlet algorithm with a time step of $\delta t = 0.01\sigma(m/k_\mathrm{B}T)^{1/2}$ where m is the (arbitrary) mass of the particles – we used $m = 1$. The choice of m does not affect the simulation results which we report. We use a semi-grand canonical ensemble where salt is allowed to enter the gel. In this grand canonical setup we prescribe the salt concentration of the supernatant phase and also account for non-idealities in the reservoir via the excess chemical potential, similar to previous simulation setups.[4-6] At each imposed volume we then record the virial pressure inside the gel $P_\mathrm{in}(V_\mathrm{gel})$. In order to find the swelling equilibrium of the gel we simulate the gel at different volumes and record pressure volume curves. We then find the equilibrium swelling via balancing the pressure in the gel with the pressure of the bath, see eqn (5). As before in the PB model, the salt concentration inside the gel is the number of negative ions $c_{\text{-},\mathrm{gel}} = N_{\text{-},\mathrm{gel}}/V_\mathrm{gel}$, where the volume of the gel V_gel is the box length cubed.

4.1 Interaction Potentials

All particles interact via the WCA potential:[7]

$$E_\mathrm{WCA}(r) = \begin{cases} 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] + \epsilon \text{ if } r < 2^{1/6}\sigma \\ 0, \text{ else} \end{cases}$$

where r is the distance between two particles. As parameters we used $\sigma = 0.355\,\mathrm{nm}$ and $\epsilon = 1\ k_\mathrm{B}T$.

Bonds between particles in the polymers are described via the FENE potential:[3]

$$E_\mathrm{FENE}(r) = -\frac{1}{2}k_\mathrm{FENE}R_\mathrm{max}^2 \ln\left(1 - \left[\frac{r}{R_\mathrm{max}}\right]^2\right),$$

where R_max is the maximal stretching of the bond, k_FENE a constant that defines the strength of the bond. If the particle distance r approaches ΔR_max the bond potential diverges. As parameters we used $k_\mathrm{FENE} = 30.0\,k_\mathrm{B}T/\sigma^2$ and $R_\mathrm{max} = 1.5\sigma$.

The Coulomb interaction energy of two charges is given by:

$$E_{\mathrm{el}}(r) = \lambda_{\mathrm{B}} k_{\mathrm{B}} T \frac{z_1 z_2}{r}, \tag{6}$$

where $z_1 = 1$ and $z_2 = 1$ are the valencies of the two charges, $k_{\mathrm{B}}T$ the thermal energy and λ_{B} the Bjerrum length. In our MD simulations this interaction is handled via the P3M algorithm.[1] As parameter we used the Bjerrum length of water $\lambda_{\mathrm{B}} = 2.0\sigma = 0.71\,\mathrm{nm}$.

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