

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

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

10 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

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

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

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

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

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

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

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