# Anisotropic Contraction of Fiber-reinforced Hydrogels: Supplementary Information

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# I. THE UPPER BOUND OF THE CONTRACTION ANISOTROPY FOR A UNIAXIALLY CONSTRAINED HYDROGEL WITHOUT PRESTRAIN

To prove Eq. 13 in the main text, we firstly show that the  $\chi$  value of the uniaxially constrained hydrogel is always larger than that of the free hydrogel at the same  $\phi$ when  $\phi > \phi_c$ . Let  $\chi$  and  $\chi'$  denote the Flory parameter for the free hydrogel and the uniaxially constrained hydrogel respectively;  $\chi$  and  $\chi'$  intersect at  $\phi_c$  as shown in Fig. 1b. According to Eq. 5 and 6 in the main text,  $\chi$ and  $\chi'$  differ by

$$\chi - \chi' = \frac{N\nu}{V_m \phi^2} \left(\frac{1}{\lambda_{\parallel}} - \phi^{1/3}\right) \tag{S1}$$

which suggests that  $\chi < \chi'$  for arbitrary  $\phi > \phi_c$  and vice versa. If the initial state of the contraction has no prestrain, i.e.,  $\phi'_i = \phi_i = \phi_c$ ,  $\phi'_f$  and  $\phi_f$  must be larger than  $\phi_c$ . Thus

$$\chi'(\phi_f) > \chi(\phi_f) = \chi'(\phi'_f).$$
(S2)

Since  $\chi'$  is monotonic as a function of  $\phi$ , we obtain  $\phi_f > \phi'_f$  which leads to  $(\phi'_f/\phi'_i)^{1/2} < (\phi_f/\phi_i)^{1/2} = \alpha_0^{-3/2}$ .

## II. FLORY-HUGGINS PARAMETER OF POLY(ETHLYENE OXIDE) (PEO) IN AQUEOUS SOLUTIONS

We describe the PEO behavior in aqueous solutions with the Dormidontova's model [1] which is briefly introduced as follows. The free energy of PEO/water solutions is essentially formulated within the framework of Flory-Huggins theory. Each PEO chain has N monomers of volume  $v_p$ , and each water molecule is represented as a monomer of volume v, which is used as the reference volume for the free energy. The translational entropy contribution of the PEO solutions follows the same form as the Flory-Huggins theory:

$$\frac{F_{\text{trans}}}{kT} = \frac{v}{Nv_p}\phi\ln\phi + (1-\phi)\ln(1-\phi)$$
(S3)

The interaction energy between PEO monomers and water without the hydrogen bondings involved is given by

$$\frac{F_{\rm int}}{kT} = \chi \phi (1 - \phi) \tag{S4}$$

Here  $\chi$  possesses the standard form A + B/T. According to the Dormidontova's model, the free energy due to the hydrogen bondings is presented in the form:

$$\frac{F_{\rm HB}}{kT} = 2\phi \frac{v}{v_p} \left[ p \ln p + (1-p) \ln(1-p) - p \frac{\Delta f_p}{kT} \right] 
+ 2(1-\phi) \left[ q \ln q + (1-q) \ln(1-q) - q \frac{\Delta f_w}{kT} \right] 
+ 2(1-\phi) \left( 1 - q - p \frac{\phi}{1-\phi} \frac{v}{v_p} \right) \ln \left( 1 - q - p \frac{\phi}{1-\phi} \frac{v}{v_p} \right) 
- 2(1-\phi) \left( q + p \frac{\phi}{1-\phi} \frac{v}{v_p} \right) \ln \frac{2(1-\phi)}{e} 
- 2(1-\phi) \left[ q_0 \ln q_0 - q_0 \frac{\Delta f_w}{kT} + 2(1-q_0) \ln(1-q_0) - q_0 \ln \frac{2}{e} \right]$$
(S5)

where p represent the average fraction of hydrogen bonds between PEO and water, and q is the average fraction of association in water;  $q_0$  is the value of q at  $\phi = 0$ , i.e., the average fraction of association in pure water.  $\Delta f_p$  is the free energy of the formation of each PEO-water hydrogen bond, and  $\Delta f_w$  is the free energy of the formation of each water-water hydrogen bond. It is noteworthy that Eq. S5 is obtained by subtracting the free energy of pure PEO ( $\phi = 1$ ) and water ( $\phi = 0$ ) from the mixed state. The detailed derivation of Eq. S5 can be referred to Ref. [1, 2]. The total free energy per lattice site is therefore the sum of Eq. S3, S4 and S5:

$$F = F_{\rm trans} + F_{\rm int} + F_{\rm HB} \tag{S6}$$

p and q must satisfy  $\partial F/\partial p = 0$  and  $\partial F/\partial q = 0$  to minimize the total free energy, which delivers

$$\frac{p}{2(1-p)\left[(1-\phi)(1-q) - p\phi\frac{v}{v_p}\right]} = \exp\left(\frac{\Delta f_p}{kT}\right) \quad (S7)$$

$$\frac{q}{2(1-q)\left[(1-\phi)(1-q) - p\phi\frac{v}{v_p}\right]} = \exp\left(\frac{\Delta f_w}{kT}\right) \quad (S8)$$

The  $\phi$ -dependent  $\chi$  of PEO in aqueous solutions can be obtained by comparing Eq. S3-S5 with Eq. 3 in the main text, and subsequently  $\overline{\chi}$  can be derived as:

$$\overline{\chi} = \chi + \frac{2}{\phi} \left( p \frac{v}{v_p} - q \right) + \frac{2}{\phi^2} \left[ q - q_0 + \ln \frac{q}{q_0(1-\phi)} \right]$$
(S9)

Eq. S9 exhibits a non-trivial dependence of  $\overline{\chi}$  on  $\phi$  which is in good agreement with experiments [2]. Using Eq. S9 to replace  $\chi$  in Eq. 5 and 6 of the main text, and incorporating Eq. S7-S8, we are able to solve the  $T \sim \phi$  relations for PEO hydrogels as shown in Fig. S2. All the parameters for our calculations are obtained from Ref. [1].

### **III. FINITE ELEMENT SIMULATIONS**

The finite element simulations are performed using ABAQUS/Standard. The hydrogel matrix is meshed with C3D8R elements. In all the simulations the mesh density is validated in mesh convergence studies.

#### A. Verification of the UHYPER

The UHYPER subroutine is verified in both a free swelling hydrogel (Fig. S3a) and a swelling hydrogel under uniaxial constraint (Fig. S3b). The simulations are performed with  $N\nu/V_m = 0.005$ , and  $\lambda_{\parallel} = 2.0$ . The simulations results show perfect agreement with the analytical results from Eq. 5, 6 and 7 in the main text.

# B. Transverse contraction of the prestretched fiber-reinforced hydrogel at L/l = 1

We have also performed simulations for a prestretched fiber-reinforced hydrogel at L/l = 1 by varying the transverse fiber-fiber distance. The simulations are performed with d = 10 nm,  $N\nu/V_m = 10^{-4}$ ,  $\phi_c = 5.0^{-3}$ ,  $\phi_i = 2.5^{-3}$ and  $\alpha_0 = 0.8$ ; thus the hydrogel undergoes 100% longitudinal prestrain before contraction. The simulation results in Fig. S4 show similar decreasing behavior as Fig. 5 in the main text.

#### C. Stress concentration at the fiber ends

The stress concentration is observed at the fiber ends due to the strong reinforcement of the rigid fiber, as shown in Fig. S5. When D/d = 2.5 (see Fig. S5a), moderate stress concentration occurs at the fiber end; the stress near the whole fiber is also substantially larger than the rest of the hydrogel due to the reinforcement of the fiber. Thus the longitudinal contraction is highly restricted when D/d is relatively small. The stress concentration near the fiber end is even more remarkable at D/d = 6.0 (see Fig. S5b). However, large portion of the hydrogel with low stress also presents in Fig. S5b, which counteracts the large strain energy introduced by the local stress concentration near the fiber. Overall, the longitudinal contraction is energetically favored at high D/d.

#### **D.** The contraction anisotropy at different $N\nu/V_m$

Figure S6 shows that the maximum contraction anisotropy occurs at the same value of D/d when varying  $N\nu/V_m$ . The overall elevation of A with decreasing  $N\nu/V_m$  agrees with the numerical calculation at  $\varepsilon_{\parallel} = 0$ in Fig. 2 of the main text.

[1] E. E. Dormidontova, Macromolecules 35, 987 (2002).

<sup>[2]</sup> V. A. Baulin, Polymères neutres solubles dans l'eau : Origine et signatures de la dépendance en concentration du paramètre de Flory chi, Theses, Université Joseph-Fourier

<sup>-</sup> Grenoble I (2003), membres de Jury Marcel Vallade Mohamed Daoud Albert Johner Loic Auvray Avi Halperin.



FIG. S1. Schematic  $\chi \sim \phi$  plot of a uniaxially constrained hydrogel (red curve) undergoing a stronger volumetric contraction  $(\phi'_f/\phi'_i > \phi_f/\phi_i)$  than a free-shrinking hydrogel (blue curve) with  $\epsilon_{\parallel} > 0$ .



FIG. S2. Contraction of PEO hydrogels upon increasing temperature. The contraction of a free-shrinking (blue curve) and a uniaxially constrained (red curve) PEO hydrogel as the temperature increases from  $T_i$  to  $T_f$ .





FIG. S3. Verification of the implementation of the finite element user-defined subroutine. (a)  $\chi \sim \phi$  plot of a free swelling hydrogel. (b) The stress  $\sigma_3$  along the constrained direction for a uniaxially constrained hydrogel. At  $\phi = \phi_c$ , the stress vanished as expected. The inset illustrate the corresponding  $\chi \sim \phi$  curve of the uniaxially constrained hydrogel.



FIG. S4. The transverse contraction ratio of the prestretched fiber-reinforced hydrogel as a function of the reduced transverse fiber-fiber distance (D/d) at L/l = 1



FIG. S5. The von Mises stress distribution at (a) D/d = 2.5 and (b) D/d = 6.0. Only one-eighth of unit cell is shown in the figure due the symmetry of the model.



FIG. S6. The contraction anisotropy at different  $N\nu/V_m$ . L/l = 1.25.