Modelling of a hydrogel diffraction grating used for pH-sensing

Modélisation d'une grille de diffraction d'hydrogel pour la mesure du pH

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A R T I C L E   I N F O

A B S T R A C T

pH-Sensitive hydrogels are networks of polymers that can imbibe a solution and swell. They are used in many smart engineering devices. One of such applications is a diffractometric biochemical sensor. This sensor is composed of a hydrogel grating fixed on a hard substrate that can swell due to pH changes. The aim of the present study is to develop a numerical model of such a bi-material device used to measure pH value of a solution.

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R É S U M É

Les hydrogels sensibles au pH sont des réseaux de polymères qui gonflent lorsqu'ils sont immergés dans une solution. Ils sont présents dans de nombreux systèmes d'ingénierie intelligents. L'application retenue est un capteur biochimique utilisant la diffractométrie. Ce capteur se déforme en fonction des variations du pH. Il se compose d'une grille d'hydrogel fixée à un substrat rigide. L'objectif de cette étude est de développer un modèle numérique d'un tel système de bi-matériaux, système utilisé pour mesurer le pH d'une solution.

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1. Introduction

Due to the intrinsic coupling between their mechanical behaviour and multiphysics properties, active materials are widely used in modern technologies, and attract a substantial modelling effort, see, e.g., [1–4]. An important place among these astonishing materials is taken by smart hydrogels that are networks of polymers that can imbibe a solution and swell due to different physical or chemical stimuli. Thanks to this feature, such hydrogels are widely used in many fields such as micro-fluidics [5], sensors [6,7], actuators [8], medicine [9], optical devices [10], and others. Their deformation can strongly depend on external stimuli such as pH, light, temperature, magnetic field and others, or, more generally, on the intensity

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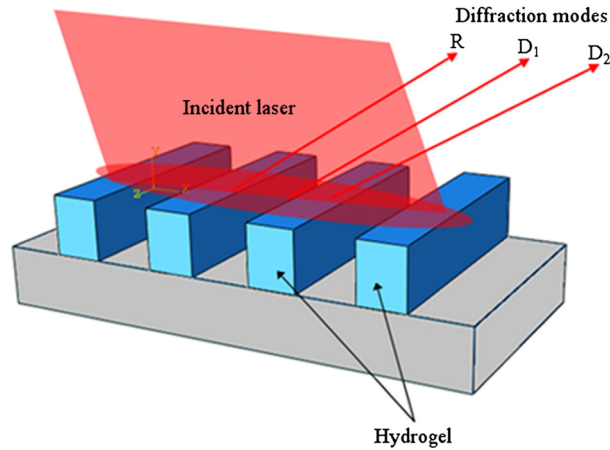*E-mail address:* labesse@moniut.univ-bpclermont.fr (F. Labesse-Jied).

Fig. 1. (Colour online.) A hydrogel diffraction grating used for pH-sensing. Each hydrogel stripe swells with increasing pH.
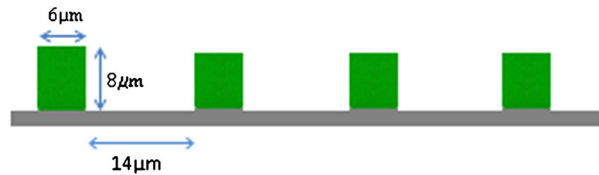

Fig. 2. Initial geometry used in the finite element modelling of the hydrogel diffraction grating. The plane top of each stripe is supposed to have a very thin but rigid coating. In the finite-element analysis, all top nodes are linked correspondingly.

of the physical or chemical stimulus. Note, for example, that in medical applications, measuring pH or glucose or antigen concentration of the solution is of great importance. Recently, a diffractometric biochemical sensing device using smart hydrogels has been reported [11]. It is based on a hydrogel reflective diffraction grating on a hard substrate, which can be used for a precise measurement of pH.

The aim of this paper is to propose a coupled mechanical and photonic model of such a smart device, based on recent advances in mechanical modelling of hydrogels. To do that, we follow the theory of inhomogeneous swelling of a pH-sensitive hydrogel, proposed in [12]. A pH-sensitive hydrogel grating is a functional part of the sensor. This grating is situated on a hard substrate and can swell or shrink as pH changes. The hydrogel is characterized by a free-energy function taking into account the stretching of the network, mixing the solvent with the network, mixing ions with the solvent, and dissociation of the acidic groups [13–15]. A model based on both a reflected beam analysis and calculations of mechanical displacements of the studied system is developed. An analysis of the reflected beam intensities for different hydrogel grating heights and incident angles coupled with the calculations of the hydrogel grating vertical displacements for different pH values provides a way to link the reflected beams measurements with the pH values. The presented model of the mechanical and photonic response of the smart hydrogel grating explains how such a smart device can be used for pH-detection.

2. Hydrogel reflective diffraction grating on a substrate

Consider a pH-sensitive hydrogel diffraction grating used for pH sensing (Fig. 1). This hydrogel grating is situated on a rigid substrate and can swell or shrink as pH changes (Figs. 2–3). The top of each stripe is supposed to have a very thin, but rigid coating.

To model the considered system, we follow the nonlinear field theory proposed by Marcombe et al. [12] for an inhomogeneous constrained swelling of a pH-sensitive hydrogel. Consider a network of crosslinked polymer-bearing acidic groups that is in equilibrium with an aqueous solution and mechanical forces. We remind briefly the basic assumptions underlying this theory. Let $\mathbf{X}$ be the coordinate vector of a particle of hydrogel in the reference state, which, after swelling, moves to a place with coordinate $\mathbf{x}$. Thus, the deformation field is described by the function $\mathbf{x} = \mathbf{x}(\mathbf{X})$, and the deformation gradient $\mathbf{F}$ is

$$F_{iK} = \frac{\partial x_i(\mathbf{X})}{\partial X_K} \tag{1}$$

Let $\bar{n}_S$, $\bar{n}_-$, $\bar{n}_+$ and $\bar{n}_{H^+}$ be the number of solvent molecules, negative ions (co-ions), positive ions (counterions) and hydrogen ions in the external solution. Their electrochemical potentials are denoted by μ_S, μ_-, μ_+ and μ_{H^+}, respectively. We define $dV(\mathbf{X})$ as a volume element in the reference state and $dA(\mathbf{X})$ as an area element. Also, let $B_i(\mathbf{X})dV(\mathbf{X})$ be the external mechanical volume force applied on the element $dV(\mathbf{X})$ and $T_i(\mathbf{X})dA(\mathbf{X})$ be the external force applied on the area
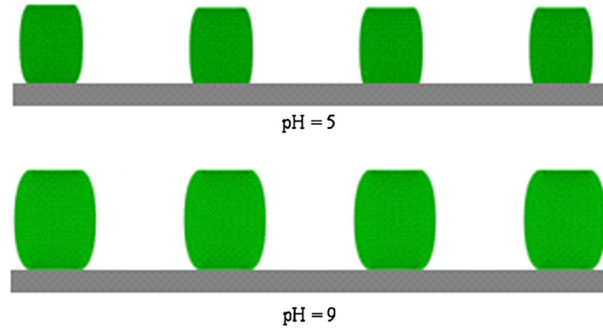
Fig. 3. Examples of the calculated final geometry of the hydrogel diffraction grating for a) pH = 5 and b) pH = 9. The top of each stripe remains plane, horizontal, and its nodes have the same vertical displacement. The hydrogel grating with its changing height acts as an optical element.

element. The variation of the Helmholtz free energy of the considered system, which is composed of the hydrogel, external solution and external forces, is associated with small variations of $\mathbf{x}(\mathbf{X})$, $\bar{n}_S$, $\bar{n}_-$, $\bar{n}_+$ and $\bar{n}_{H^+}$, and it is equal to the sum of the variation of the free energy of the hydrogel $\int \delta W \mathrm{d}V$, of the external solution $\mu_S \delta \bar{n}_S + \mu_+ \delta \bar{n}_+ + \mu_- \delta \bar{n}_- + \mu_{H^+} \delta \bar{n}_{H^+}$ and of the potential energy of the mechanical volume and area forces $\int B_i \delta x_i \mathrm{d}V + \int T_i \delta x_i \mathrm{d}A$. If the system is in equilibrium, the variation of free energy equals zero:

$$\int \delta W \mathrm{d}V + \mu_S \delta \bar{n}_S + \mu_{H^+} \delta \bar{n}_{H^+} + \mu_+ \delta \bar{n}_+ + \mu_- \delta \bar{n}_- - \int B_i \delta x_i \mathrm{d}V - \int T_i \delta x_i \mathrm{d}A = 0 \tag{2}$$

Let us denote by $C_S(\mathbf{X})$, $C_-(\mathbf{X})$, $C_+(\mathbf{X})$ and $C_{H^+}(\mathbf{X})$ the nominal concentrations, i.e. their number divided by the volume of the hydrogel in the reference state, of the solvent molecules, the co-ions, the counterions and the hydrogen ions, respectively. The hydrogel can obtain only the solvent molecules, the co-ions, the counterions from the external solution, so we get:

$$\int \delta C_\alpha(\mathbf{X}) \mathrm{d}V + \delta \bar{n}_\alpha = 0 \quad (\alpha = S, -, +) \tag{3}$$

The hydrogel contains acidic groups-AH that can dissociate into fixed charges A^- attached to the network and the mobile hydrogen ions H^+. So, the hydrogen ions in the hydrogel can be either produced by the acidic group dissociation from the polymer chain or come from the external solution. This means that we have the following relation:

$$\int \delta C_{H^+}(\mathbf{X}) \mathrm{d}V + \delta \bar{n}_{H^+} - \int \delta C_{A^-}(\mathbf{X}) \mathrm{d}V = 0 \tag{4}$$

Denote by f the number of acidic groups AH attached to the polymer network which is divided by the number of monomers in the network. Let Ω be the volume per monomer. The total number of acidic groups is equal to the sum of two numbers, that of the associated acidic groups AH and that of the fixed charges A^-:

$$C_{AH}(\mathbf{X}) + C_{A^-}(\mathbf{X}) = f/\Omega \tag{5}$$

Further, the electroneutrality of the gel and of the external solution can be assumed when the size of the gel is much larger than the Debye length [12]:

$$C_{A^-}(\mathbf{X}) + C_-(\mathbf{X}) = C_{H^+}(\mathbf{X}) + C_+(\mathbf{X}) \tag{6}$$

$$\bar{n}_+ + \bar{n}_{H^+} = \bar{n}_- \tag{7}$$

Assuming that the amount of the ions inside the hydrogel is much smaller than the amount of water molecules in the hydrogel and using the molecular incompressibility assumption, we can write that the total volume of the gel is equal to the sum of the volume of the dry polymer and the volume of the water

$$1 + \Omega_S C_S = \det \mathbf{F} \tag{8}$$

where Ω_S is the volume of a single molecule of water.

Following [12–15], we assume that the free-energy density of the gel is a sum of the following contributions:

$$W = W_{net} + W_{sol} + W_{ion} + W_{dis} \tag{9}$$

In (9), W_{net} is due to the stretching of the network, W_{sol} corresponds to the mixing of the solvent with the network, W_{ion} describes the mixing of ions with the solvent, and W_{dis} is related to the dissociation of the acidic groups. For the free energy associated with the stretching of the network, we use the Gaussian-chain model:

$$W_{\text{net}} = \frac{1}{2} NkT \big[F_{iK} F_{iK} - 3 - 2 \log(\det \mathbf{F}) \big] \tag{10}$$

in which N is the number of polymer chains divided by the volume of the dry network and kT is the temperature in the unit of energy.

The free energy associated with the mixing of the polymers with the solvent can be presented under the form:

$$W_{\text{sol}} = \frac{kT}{\Omega_S} \left[\Omega_S C_S \log\left(1 + \frac{1}{\Omega_S C_S} \right) + \frac{\chi}{1 + \Omega_S C_S} \right] \tag{11}$$

where χ is a dimensionless measure of the mixing enthalpy.

The free energy associated with the mixing of the ions with the solvent is:

$$W_{\text{ion}} = kT \left[C_{\text{H}^+} \left(\log \frac{C_{\text{H}^+}}{c_{\text{H}^+}^{\text{ref}} \det \mathbf{F}} - 1 \right) + C_+ \left(\log \frac{C_+}{c_+^{\text{ref}} \det \mathbf{F}} - 1 \right) + C_- \left(\log \frac{C_-}{c_-^{\text{ref}} \det \mathbf{F}} - 1 \right) \right] \tag{12}$$

where c_α^{ref} is a reference value of the concentration of different species.

Finally, the free energy due to the dissociation of the acidic groups is taken to be

$$W_{\text{dis}} = kT \left[C_{\text{A}^-} \log\left(\frac{C_{\text{A}^-}}{C_{\text{A}^-} + C_{\text{AH}}} \right) + C_{\text{AH}} \log\left(\frac{C_{\text{AH}}}{C_{\text{A}^-} + C_{\text{AH}}} \right) \right] + \gamma C_{\text{A}^-} \tag{13}$$

with γ the enthalpy due to the dissociation of the acidic groups.

Due to conditions (3)–(8), the number of independent fields that define the state of the swollen hydrogel is reduced to four: for example, $x_i(\mathbf{X})$, $C_-(\mathbf{X})$, $C_+(\mathbf{X})$ and $C_{\text{H}^+}(\mathbf{X})$. Therefore, the nominal density of free energy can be written as a function of four independent variables:

$$W = W(\mathbf{F}, C_+, C_-, C_{\text{H}^+}) \tag{14}$$

Without entering into further details of the used theory, let us just mention that the variational statement (2) for the inhomogeneous swelling of the pH-sensitive hydrogel was further implemented, see [12], in a finite-element code ABAQUS. This was done using the Legendre transformation of the free-energy function:

$$\hat{W} = W - (\mu_+ - \mu_{\text{H}^+})C_+ - (\mu_- + \mu_{\text{H}^+})C_- - \mu_S C_S \tag{15}$$

Inserting this equation into (2) and using conditions (3)–(8), one obtains

$$\int \delta \hat{W} \, dV = \int B_i \delta x_i \, dV + \int T_i \delta x_i \, dA \tag{16}$$

where $\hat{W}$ is a new free energy of the pH-sensitive gels, which can be directly implemented into most finite-element analysis programs. As it was shown in [12], taking into account the equations of state, the new function of free energy depends only on the deformation gradient and on the concentrations of positive ions and hydrogen ions in the external solution:

$$\hat{W} = \hat{W}(\mathbf{F}, \bar{c}_{\text{H}^+}, \bar{c}_+) \tag{17}$$

This free-energy function has been implemented in [12] into a subroutine UHYPER in ABAQUS which we use to analyse grid swelling. Note that the swelling of the hydrogels is a rather slow process, see, e.g., [11]. To exclude the notion of time from our discussion, we assume, while changing the pH values used in the calculations, that the equilibrium in the system for each given pH value had been achieved. Note also that such an assumption is commonly used in the literature and that it corresponds in our case to the experimental conditions reported in [11].

In our calculations, we used an 8-node biquadratic plane-strain quadrilateral, hybrid, linear pressure, reduced integration element (CPE8RH). The initial geometry of the studied hydrogel diffraction grating (with an initial height $h_0 = 8$ μm, and the width of a stripe $b = 6$ μm) is presented in Fig. 2.

The bottom of each hydrogel stripe is fixed on a rigid substrate. The top of each stripe remains plane, horizontal, and its nodes are linked in such a way that they all have only a vertical displacement, which is the same for all nodes of its top surface. In other words, all nodes of top surface of each stripe do not have any horizontal displacement, and they have the same vertical one. The sidewalls of each stripe are free from forces. The change in the hydrogel stripe geometry due to pH changes is depicted in Fig. 3. Thus, the functional part of the diffraction grating, which is the top surface of the swelling hydrogel diffraction grating, is composed of the unchanging top surfaces of each stripe, which can move upwards when the gel swells and downwards when the gel shrinks. Its height change, i.e. the hydrogel vertical displacement, serves as the only parameter responsible for the changing photonic behaviour of the grating. Note that this numerical model and the boundary conditions we use are consistent with the experimental configuration described in [11].

In calculations, the following parameters are taken for the pH-sensitive hydrogel [12]: $Nv = 0.001$, where N is the number of polymer chains per unit of volume of the dry network and v is the volume per monomer, $\chi = 0.1$, the mixing enthalpy of the polymers and the solvent, and $f = 0.05$, the number of acidic groups on a polymer chain divided by the
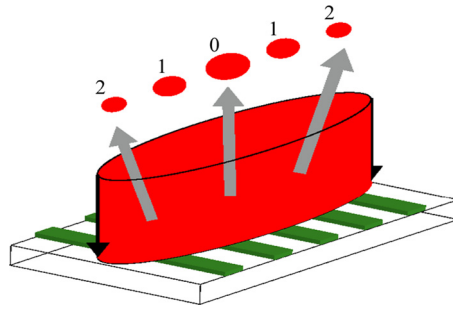
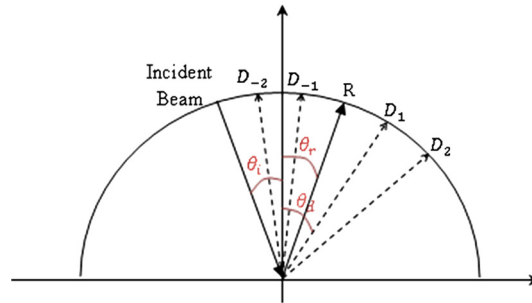**Fig. 4.** Perfect diffraction grating.

Fig. 5. Representation of different diffraction modes ($R, D_{-1}, D_1, D_{-2}, D_2$).

total number of monomers on the chain. A commonly accepted value of the pK_a (dissociation of carboxylic acids) is 4.25. As the pH value increases gradually from pH $= 2$ to pH $= 9$ in steps of 0.5 pH, the geometry and the deformation of the hydrogel grating is calculated (Fig. 3).

We compare the calculated deformation with the experimental optical micrographs of the hydrogel grating presented in [11] and we note a good visual agreement between our calculations and the experiment. Further comparison between the calculated data and available experimental results is presented in the final part of this paper.

The hydrogel grating with its changing height acts as an optical element (Fig. 4). This periodic structure transforms the incident beam into a reflected and several diffracted beams. The angle of the reflected beam θ_r is equal to the angle of the incident beam θ_i. The other diffraction modes (D_{-1}, D_1, D_{-2}, D_2) diffract with other angles, different from the incident angle (Fig. 5).

For a perfect diffraction grating (Figs. 4–5), the intensity of the 0th- and first-order diffraction modes can be represented by (R) and (D_1), respectively [16]:

$$R \infty \cos^2\left(2\pi\frac{nh}{\lambda}\right) \tag{18}$$

$$D_1 \infty \sin^2\left(2\pi\frac{nh}{\lambda}\right) \tag{19}$$

Here, n represents the refractive index of the medium given by the designers of this experimental device [11] ($n = 1.33$ for solution), h the height of the grating and λ the wavelength of the laser beam (632.8 nm). For the thickness of the grating is large compared to λ, the intensities of reflected and diffracted beams are quasi-periodic functions of both the angle of incidence and the thickness of the grating controlled by the phase difference $\Delta\varphi$ between two beams deflected front and bottom sides of the gratings, which can be represented by:

$$\Delta\varphi \infty \frac{2\pi h}{\lambda} f(\theta_i) \tag{20}$$

In (20), $f(\theta_i)$ is a function that depends on the incident angle θ_i (Fig. 6). As can be seen from the above Eq. (20), this phase difference depends on the incident angle θ_i and on the height of the grating h. Using Eqs. (18)–(20), we deduce that the period of oscillations of the reflected beam intensity as a function of incident angle depends on the height of the grating.

Using [17], we consider an incident beam of light on a grating made of pH-sensitive hydrogel, and we can calculate the dependencies of the intensities of different reflected beams ($R, D_{-1}, D_1, D_{-2}, D_2$) on the incident angle θ_i for any hydrogel grating height change induced by a certain pH change. All obtained dependencies are periodic and have a certain period, which is a function of the hydrogel grating height change, which, in turn, depends directly on the current pH value. Note that the evolution of the reflective beam intensities is equivalent for S- and P-polarization. Therefore, further results are
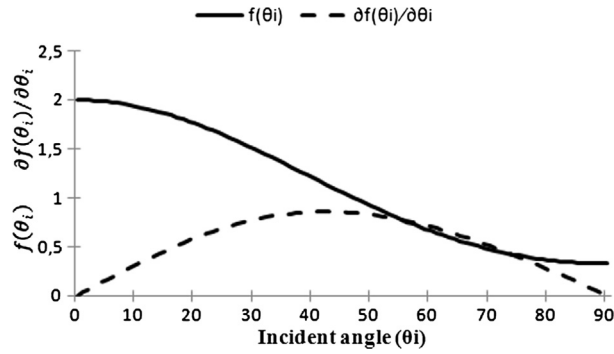
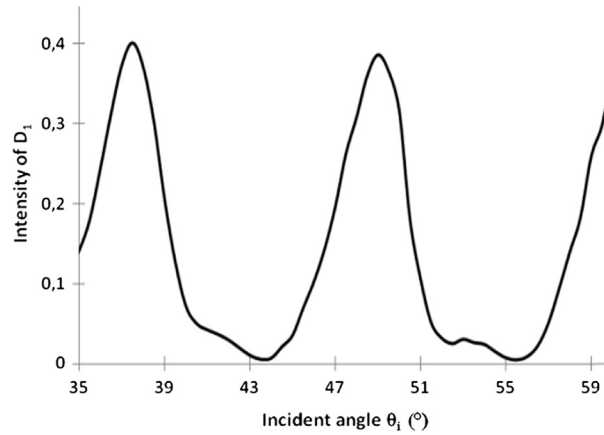**Fig. 6.** $f(\theta_i)$ and $f'(\theta_i)$ *versus* the incident angle.

Fig. 7. Example of dependency of (D_1) intensity on different values of the incident angle θ_i.
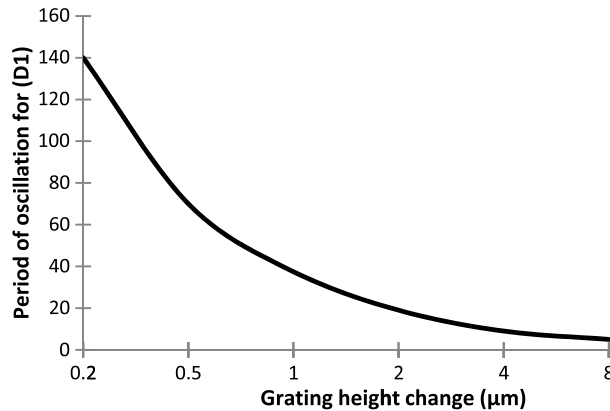

Fig. 8. Period of oscillation for the diffracted beam (D_1) vs. hydrogel grating vertical displacement (grating height change).

presented for S-polarization. In Fig. 7, we plot as an example the dependency of the diffracted beam's (D_1) intensity on the incident angle θ_i. Such dependencies can be both measured experimentally or calculated numerically using our approach for any hydrogel grating height change induced by a certain pH change. This means that the pH value can be determined by means of our model if the dependency of the diffracted beam's (D_1) intensity on the incident angle θ_i is measured. To be able to do that, we calculated the period of oscillation for the diffracted beam (D_1) for any possible hydrogel grating vertical displacement. These results are plotted in Fig. 8.

On the other hand, we calculated the dependency between the vertical displacement of the hydrogel grating and pH (Fig. 9). The obtained numerical results presented in Figs. 8 and 9 suggest that the reflected beam measurements can be used to find the corresponding pH value. Assume that an incident light beam is applied with different angles on the diffraction grating. For each incident angle, the diffracted intensity (D_1) can be measured optically. Let, for example, the results of this measurement be the results presented in Fig. 7. We can further analyse these results as follows. First, we
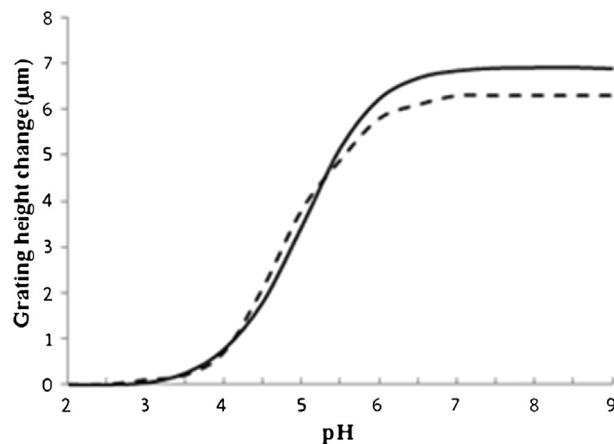
Fig. 9. Calculated dependency between the hydrogel grating vertical displacement and the pH (solid line) and the corresponding experimental curve [11] (dashed line).

find the period of oscillation of the reflected beam intensity (D_1), measured between two minima. In the case of Fig. 7, it is equal to 12°. Then we use the calculated results presented in Fig. 8 and determine that, for the found oscillation period 12°, the corresponding height change of the hydrogel grating is equal to 3.6 μm. Finally, we use the results presented in Fig. 9 to determine the pH value. If we use the solid line, calculated numerically, we obtain pH = 5.05. If we use the dashed line, which represents the available experimental result [11] for the hydrogel grating, we get a slightly different pH value. Let us comment on this difference and on the accuracy of this calculation. If the dashed line based on experimental measurements [11] is used instead of the calculated solid one, we arrive at the value pH = 4.95. A comparison with the previously found pH value shows a very good correspondence between the theoretical and the experimental result in this particular case. Note also that Fig. 9 generally demonstrates a good qualitative correspondence of the theoretical and the experimental pH-versus-height-change plots for a wide range of pH values for the given hydrogel diffraction grating. Thus we hope that our coupled mechanical and photonic model can provide a simple and relatively accurate tool for linking the reflected beams measurements with the pH values, especially for the cases when no experimental results are available.

3. Conclusion

A coupled mechanical and photonic model of a diffractometric biochemical sensing device is proposed. This smart device is based on a hydrogel reflective diffraction grating on a hard substrate and can be used for measuring pH. The functional part of this bi-material device is a hydrogel grating that is capable of swelling or shrinking due to pH changes. We describe its mechanical behaviour using some recent advances in mechanical modelling of hydrogels [12]. A numerical model based on both a reflected beam analysis and calculations of mechanical displacements of the studied system is developed. An analysis of the reflected beam intensities for different hydrogel grating heights and incident angles coupled with the calculations of the hydrogel grating vertical displacements for different pH values provides a way to link the reflected beams measurements with the pH values. Calculations are performed to illustrate our approach.

Acknowledgements

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