Design Considerations for Electrostatic Microvalves With Applications in

# Poly(dimethylsiloxane)-based Microfluidics

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# **Supplementary Information**

### 1. Assumptions in deriving expressions for static stiffness of membrane

The expressions for stiffness of a membrane (eqn (1)) are derived based on the following assumptions (in italics), each followed by its justification.

- The membrane is homogenous, uniformly thick, and perfectly clamped at the outer edges.
   We predict that the microfabrication techniques will impose strict tolerances on material properties and dimensions, particularly membrane thickness.
- 2. *The deformation of the membrane is elastic*. Poly(dimethylsiloxane) or PDMS exhibits elastic behavior for the range of strain values experienced by the microvalve membranes discussed in this paper.<sup>1</sup>
- 3. *Membrane displacement due to transverse shear is negligible*. This assumption holds if the aspect ratio of the membrane, *i.e.*, the ratio of the diameter (or side length) to the thickness, is greater than 5.<sup>2</sup> In typical microfluidic microvalves and the microvalves discussed in this paper, the aspect ratio of the membrane will generally be greater than 10.
- 4. *The Poisson's ratios of the two layers making up the bilayer membrane are not significantly different.* Both the layers of the membrane are assumed to be of similar materials; in this paper, we assume both the layers are made of PDMS.
- 5. The expressions for static stiffness of the membrane can also be used to estimate the stiffness of the membrane during dynamic operation of microvalves. This assumption is valid as long

as the operating frequencies of the microvalve are lower than the natural frequency of the membrane, which implies that the inertial effects of the membrane can be neglected. The natural frequency of a typical membrane of a PDMS-based microvalve is approximately 5 kHz, where we have assumed that the membrane is 500  $\mu$ m in diameter and 10  $\mu$ m thick (typical dimensions of microvalves in microfluidic chips), the material properties of PDMS are as listed in Table 3 in the main text, and the natural frequency of the membrane can be estimated using the equation for natural frequency of vibration for a clamped circular diaphragm.<sup>3</sup> Dynamic operation of microvalves is mostly important in peristaltic pumps in microfluidics, in which the typical operating frequencies (100 Hz)<sup>4</sup> are much lower than the natural frequency of a typical PDMS membrane, and hence, the expressions for static stiffness are applicable to the dynamic operation of PDMS-based microfluidic microvalves in typical operating regimes.

6. We assume that the membrane is clamped along the complete outer edge. However, the sections of the membrane above the entrance and exit to the microvalve are not clamped. Hence, the values for the shape factors listed in Table 1 in the main text will be different for microvalves suspended over microchannels. In the extreme case, when the membrane side length or the diameter is the same as the channel width (*i.e.*, only half of the membrane edge is clamped), then the membrane behaves as a doubly-clamped (fixed-fixed) wide beam and the analytical expressions for membrane stiffness overestimate the spring constant of the membrane. Specifically, the membrane stiffness predicted by eqn (1) in the main text is approximately 2.67 times larger than the stiffness of a doubly-clamped beam. This overestimation of stiffness would result in the predicted actuation potential to be 1.6 times greater than the actual value (eqn (2)). Hence, the shape factors (Table 1) can still be used to

calculate the membrane stiffness and from that the actuation potential for different microvalve configurations, knowing that the maximum overestimation of the potential is approximately 60%, but typically much less, on the order of 10 - 20%.

## 2. Expression for $K_{post}$ , a factor to account for presence of post in a membrane

To account for the presence of a cylindrical support post, we model the membrane as an annulus clamped at the external edges, where the central portion of the membrane, represented by the post, is rigid (non-deformable) and constrained to move only in the membrane out-of-plane direction. The expression for  $K_{post}$  is derived based on the expression for stiffness of an annular membrane with a guided central part,<sup>5</sup> and is given as follows

$$K_{post} = \frac{1}{64f(b/a)}$$
  

$$b = D_{post}/2; \ a = L_e/2$$
  

$$f\left(\frac{b}{a}\right) = \frac{C_2 L_{14}}{C_5} - L_{11}$$
  

$$C_2 = \frac{1}{4} \left[ 1 - \left(\frac{b}{a}\right)^2 \left(1 + 2\ln\left(\frac{a}{b}\right)\right) \right]$$
  

$$C_5 = \frac{1}{2} \left[ 1 - \left(\frac{b}{a}\right)^2 \right]$$
  

$$L_{11} = \frac{1}{64} \left[ 1 - 4\left(\frac{b}{a}\right)^2 - 5\left(\frac{b}{a}\right)^4 - 4\left(\frac{b}{a}\right)^2 \left(2 + \left(\frac{b}{a}\right)^2 \ln\left(\frac{a}{b}\right)\right) \right]$$
  

$$L_{14} = \frac{1}{16} \left[ 1 - \left(\frac{b}{a}\right)^4 - 4\left(\frac{b}{a}\right)^2 \ln\left(\frac{a}{b}\right) \right]$$

where

 $D_{post}$  diameter of the post

$$L_e$$
 equivalent planar dimension of the membrane (side length or diameter).

#### 3. Assumptions in deriving expressions for actuation potential of a microvalve

The expressions for actuation potential of a microvalve (eqn (2)) are derived based on the following assumptions, each followed by its justification.

- 1. The fringing electric fields around the edges of the plates are assumed to be negligible. These fringing electric fields do not significantly influence the capacitance between parallel plates when the electrode gap (typically ~10  $\mu$ m) is small compared to the planar dimensions of the plate (50 – 1000  $\mu$ m), *i.e.*, the length or diameter of the membrane.<sup>6</sup>
- 2. The electric field is assumed to be constant across the membrane as the membrane is deforming. This assumption is not true when the deflection of the membrane is significant compared to the electrode gap, since the electric field will be much higher at the center of the membrane compared to the edges. Calculating the actual deflection profile of the membrane due to the non-uniform electric field would entail numerical solution of non-linear partial differential equations or multi-physics simulations using finite element analysis (FEA). Alternatively, in order to capture the influence of the non-uniform electric field, the actuation potential value can be multiplied by a constant (*K<sub>nonlinear</sub>*), which can be estimated numerically or experimentally. For example, Osterberg *et al.*<sup>7</sup> computed *K<sub>nonlinear</sub>* as 0.7545 using FEA simulations, while Rollier *et al.*<sup>8</sup> assumed *K<sub>nonlinear</sub>* as 1 and observed a maximum difference of 6% between analytical predictions and experimental observations for actuation potentials. In this paper, we assumed *K<sub>nonlinear</sub>* to be equal to 1, realizing that this assumption could induce an overestimation of approximately 25 % or less in the analytical predictions of actuation potentials.

#### 4. Effect of residual stresses on design parameter space for electrostatic microvalves

To estimate the influence of residual stresses, we plot the design parameter space for the microvalves (Fig. S1), similar to that in Fig. 2 in the main text, for two different values of residual stresses – zero and 0.04 MPa (lowest residual stress measured in free-standing PDMS membranes). We plot the design parameter space for air and water only for purposes of clarity, and compute the space for a 60 V contour, as opposed to a 300 V contour in Fig. 3 in the main text.



**Fig. S1** Design parameter space for microvalves for two different values of residual stresses actuated in air and water. The design space is estimated for two different membrane thicknesses: (a)  $t_m = 5 \ \mu m$ , (b)  $t_m = 40 \ \mu m$ , and two different values of residual stresses (0 and 0.04 MPa).

From Fig. S1, it can be observed that reducing the residual stresses increases the design parameter space slightly. More importantly, minimizing the residual stresses reduces the values of the feasible diameters of the microvalves. For example, in Fig. S1a for a 15  $\mu$ m channel height, the feasible microvalve diameters decrease from 600 – 800  $\mu$ m for 0.04 MPa residual stresses to 200 – 550  $\mu$ m for zero stress. The reduced microvalve diameters will enable development of high-density microfluidic devices.

For the above comparison (Fig. S1) and comparison in Fig. 3 of main text, we assumed the residual stresses in membrane to be 0.04 MPa, which is the minimum observed residual stresses in PDMS membranes. To complete the comparison, we estimated the design parameter space with 0.15 MPa as the residual stress (the maximum observed residual stresses in PDMS membranes), and compared the space with those obtained under the assumption of no residual stresses (Fig. S2). We observed that the design parameter is further constrained by the assumption of 0.15 MPa compared to that obtained under assumption of 0.04 MPa (Fig. 2 in main text). Another interesting observation is that the effect of residual stress is lower for higher membrane thickness (40  $\mu$ m instead of 5  $\mu$ m). This reduced effect is due to the differences in relative contribution of Young's modulus and residual stresses to membrane stiffness (equation (2) in main text). The stiffness is a function of  $E_{bm}t_m^3$  and  $\sigma_0 t_m$ , where  $E_{bm}$  is the biaxial modulus,  $\sigma_0$  is the residual stress and  $t_m$  is the membrane thickness. As the thickness increases, the contribution of modulus to membrane stiffness increases at a faster rate compared to that of residual stresses. Hence, the effect of residual stresses on actuation potential and valve collapse is lower for thicker membranes.



**Fig. S2** Design parameter space for microvalves for two different values of residual stresses actuated in air and water. The design space is estimated for two different membrane thicknesses: (a)  $t_m = 5 \ \mu m$ , (b)  $t_m = 40 \ \mu m$ , and two different values of residual stresses (0 and 0.15 MPa).

#### 5. Procedures for fabrication of the microvalve and experimental details

Molds for channels and valve chambers were made by patterning SU-8 5 photoresist (Microchem Corp.) with standard photolithographic techniques onto silicon wafers. Molds for the support layer were also fabricated with standard photolithographic techniques using SU-8 50 (Microchem Corp.). To reduce adhesion between poly(dimethlysiloxane) (PDMS) and the molds, a surface treatment was performed by placing the molds in a vacuum desiccator along with several drops of (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (Gelest, Inc.), and then applying vacuum overnight.

To construct the upper layers of the valve, including the membrane with an embedded electrode, a thin layer of PDMS (20:1 of monomer-to-curing agent weight ratio, General Electric RTV 615, Hisco, Inc.) was first spin-coated onto the mold at 10,000 rpm for 50, 120, or 300 seconds (corresponding to molds with approximately 2, 4, and 7  $\mu$ m tall features, respectively) such that a thin film covered the features on the mold (Fig. S3). The film was cured in an oven at 70 °C for 1 hr and then allowed to cool at room temperature.



**Fig. S3** Schematic diagram of the soft-lithographic approach used for fabricating the electrostatic microvalves. (MWNTs - multi-walled carbon nanotubes; SDS - sodium dodecyl sulphate; PDMS – polydimethylsiloxane).

To form a thin film of multi-walled carbon nanotubes, an aqueous suspension of multiwalled carbon nanotubes or MWNTs (20-30 nm outer diameter, 10-30  $\mu$ m length, > 95 wt% purity, ash < 1.5 wt%, Cheaptubes, Inc.) with a ratio of 1 g MWNTs : 10 g sodium dodecyl sulfate : 1 mL deionized water was prepared and sonicated (Vibra-Cell VCX130PB, Sonics & Materials, Inc.) for approximately 30 min to solubilize the MWNTs. A 0.5 mL sample was then diluted into approximately 20-30 mL deionized water and stirred briefly. The dilute suspension was filtered through a membrane filter (Whatman Anopore<sup>™</sup> inorganic membrane (Anodisc<sup>™</sup>, 0.1 or 0.2 µm pore size, 47 mm diameter) that had been wet with ethanol. After the aqueous suspension had fully passed through the membrane, the MWNTs that remained on the membrane were washed with ethanol until the filtrate was free of bubbles (Fig. S3). A PDMS stamp (20:1 of monomer-to-curing agent weight ratio) was molded and brought into contact with the MWNT film. Areas in contact with the stamp were lifted off the membrane filter and then applied to the PDMS film formed previously. Pressure was applied by hand, and after lifting off the PDMS stamp, most of the MWNT film transferred to the PDMS film. Some residual MWNTs remained on the stamp. Electrical contacts were made from a slurry of PDMS (5:1 of monomer-to-curing agent weight ratio) with 10 wt% MWNTs, which was applied at two corners of the MWNT film and subsequently cured for 15 min in an oven at 70 °C.

To encapsulate the MWNT electrode, a second layer of PDMS (20:1 of monomer-tocuring agent weight ratio) was spin-coated on top of the electrode at 2400 rpm (for membranes  $35 \pm 6 \mu m$  thick) or 3000 rpm (for membranes  $25 \pm 6 \mu m$  thick) for 30 s and allowed to cure until tacky in an oven at 70 °C for 20-40 min (Fig. S3). A PDMS support layer (5:1 of monomer-to-curing agent weight ratio) that contained 50 µm tall cylindrical cavities with diameters that matched the underlying valve chambers was aligned onto the membrane. The recesses in the support layer also contained posts scaled to have diameters 20% of the underlying valve's diameter. Uncovered regions of the spin-coated PDMS layers were filled in with liquid PDMS (5:1 of monomer-to-curing agent weight ratio) and the whole assembly was cured overnight in an oven at 70 °C. The support layer sealed permanently to the membrane due to the mismatch of curing agent concentration between the layers. The valves were removed from the mold and holes were punched to the inlets of the microchannels using a sharpened 20 gauge steel needle. To complete the valve assembly, the PDMS layers were set onto a glass slide coated with a thin film of indium tin oxide (ITO), which served as the lower electrode. The ITO film was thermally evaporated onto the glass substrate at a rate of ~1.5 Å/s for a total thickness of 2500 Å. The coated glass slides were then annealed for one hour at 550 °C, resulting in a transparent, slightly colored film. The PDMS layers formed a reversible bond with the lower electrode upon contact.

To test the potentials needed to shut the valves, first the microchannels and valve chambers were filled with fluorinated oil (3M<sup>TM</sup> Fluorinert<sup>TM</sup> FC-40). Typically, this was accomplished by dispensing several drops of fluorinated oil onto the lower electrode and then placing the upper PDMS layers of the valve on top. An electrical potential was applied between the upper and lower electrodes with a DC power supply (Hewlett Packard model 6209B). One lead from the power source was attached to a wire that was inserted into the electrical contact made of PDMS and MWNT, and the second lead was attached to the film of ITO. The upper electrode was negatively polarized. The potential was increased slowly until the membrane touched the lower electrode. After all the valves on a device had been actuated, the potential was released and the device was visually inspected to see whether valves re-opened. Before repeating the experiment, the upper PDMS layers were removed from the ITO-coated glass slide and heated at 70 °C for one hour, since we found that consecutive actuations without heating led to substantial drift in the actuation potential, possibly due to the build-up of surface charge on the membrane. For the characterization shown in Figure 4 in main manuscript, a total of three devices were tested, and each valve on every device was actuated a minimum of five times to determine average values of actuation potentials. Fig. S4 shows optical micrographs of microvalves in open and closed state.



Fig. S4 Optical micrographs of microvalves in open and closed state.

# References

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