On Pore Size Variations in Membrane Networks

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Abstract

We investigate the influence of pore size variations on the performance of porous membrane filters whose pores form a network structure and undergo adsorptive fouling. We find that unless pore size variability is very large, when considered in the context of a statistically significant sample of randomly generated networks, it is less influential on key performance metrics of the membrane filters than the inherent variability of the random network generation procedure. Since random perturbations to pore sizes tend to increase overall porosity of the pore network, we also investigate the importance of initial membrane porosity by studying porosity-corrected performance scores (among equal porosity networks).

I. INTRODUCTION

Membrane filtration is an important separation process used in many industrial and commercial applications such as treatment of radioactive sludge, water purification, beer clarification [10], semiconductor and microelectronics processing [7], air filtration [11] and membrane bioreactors [3]. Membrane filters used in these applications have a wide range of architectures, ranging from single layer thin porous films to multilayered porous membranes [2, 14] to large scale continuous sheets of layered fibrous material [11, 15].

Many models to describe the underlying membrane pore structure and/or geometry have been proposed and studied in recent years. For example, there are simple theoretical models to analyze the performance of membranes composed of multiple layers of different porous materials [4, 14], or membranes with simple branched pore structures that can incorporate porosity gradients (Polyakov [16], Sanaei and Cummings [18], among many others). As recent advances in imaging techniques have greatly contributed to the ability to compare structural models to experiments [19], more sophisticated models of membrane architecture have been formulated, with a recent focus on accurate modeling of membrane filters with a network-type pore structure, for example, membranes where the solid component is comprised of fibres (so-called node-fibril type membranes) or those that transport feed through networks of capillaries [5, 6, 9].

* This work was supported by NSF Grant No. DMS-1615719.
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Our focus here is on the latter type of pore network model, and our analysis of pore size variations is based on the model introduced by Gu et al. [6]. More details of the model may be found in §2 of the present paper, but briefly, the authors construct a network model where vertices and edges represent pore junctions and throats respectively. Pore junctions are uniformly dispersed in a unit cube (in a dimensionless framework), and a pore throat connects any two junctions that are at a distance of at most $d$ but at least $d_{\text{min}}$ apart. Each pore throat is a circular cylinder of small aspect ratio, and all pore throats initially have the same radius. Hagen-Poiseuille flow is assumed in each throat and conservation of fluid flux is imposed at each junction. Only adsorptive fouling (standard blocking) of the membrane pores is modeled: foulant is advected by fluid flow in each pore throat, and foulant flux is conserved at each pore junction. Adsorptive fouling occurs within each pore throat via foulant deposition on the wall at a rate proportional to local foulant concentration. Membrane filter performance is analyzed by recording total throughput (volume of filtrate collected during the lifetime of the filter) and accumulated foulant concentration at the membrane outlet.

The primary findings by Gu et al. [6] that motivate the present work are the following relationships. Firstly, the initial porosity (pore void volume divided by total domain volume) of the network is demonstrated to be an important material feature that predicts total throughput by a power law, which holds particularly well when initial porosity $> 0.5$. Secondly, we find that the accumulated foulant concentration at the membrane outlet decays exponentially with the initial tortuosity of the network (defined as the average distance travelled by a fluid particle from membrane inlet to outlet).

In addition to membrane pore geometry, and the degree of pore connectivity considered by network models of the type discussed above, pore size variation is another important aspect of membrane filter design. This has been investigated and modelled by a number of authors, in particular regarding how it affects membrane selectivity and particle retention in a variety of applications [8, 12, 13, 17, 20]. It has not, however, been extensively studied in the context of network models for membrane filters: though such models allow for cylindrical pores with a random distribution of lengths [3, 6], random variations of the pore radii have not, to our knowledge, been considered. Accordingly, in this paper, we focus on membrane filters whose pores may be considered as a network of interconnected capillaries with different initial radii. We present a novel characterisation of the membrane pore network and model
pore size variations via a set of random initial conditions for the radii of pore throats, an approach different from the log-normal pore size distribution often assumed in applications. This method has the benefit of incurring only one additional parameter – noise amplitude, as opposed to a mean and variance in a log-normal distribution approach – while still capable of capturing effects such as inhomogeneities due to the manufacturing process. We use this network representation to investigate the effect of pore size variations on the performance of membrane pore networks, as characterized by foulant concentration and total throughput of filtrate over the filter lifetime.

The work of the present paper is outlined as follows: in §II we describe the network model setup and introduce the key performance metrics. In §III we set out our investigation strategy for pore size variation in an algorithm and declare the main nomenclature used in the analysis. In §IV we present and briefly discuss our main results, and in §V we conclude our findings.
II. SETUP: GENERAL PORE NETWORKS

In this section we construct our model of a filter membrane represented by a random network of connected cylindrical pores. In § II A we describe how we generate a network that represents the internal pore structure of a membrane filter; in §§ II B-II C we outline the governing equations for the Hagen-Poiseuille fluid flow, for the advection of foulant particles carried by the flow, and for the pore throat evolution in time; in § II D we provide the relevant scales; and in § II E we introduce two metrics to characterize the performance of a membrane filter with a specified pore network.

A. Network Generation

We describe the interior of the membrane filter by a random network of cylindrical pores, connected at pore junctions (nodes of the network). We generate a pore network by first uniformly distributing \( N_{\text{total}} \) (a large integer to be prescribed) points as the pore junctions, inside a square prism with side length \( W \), and height \( 2W \) units. We construct pore throats (or simply pores; the edges of the network) by connecting all pairs of points that lie within a distance of \( D \) but at least \( D_{\text{min}} \) apart, under a periodic metric (junctions close to a given face of the square prism may connect to points sufficiently close to the opposite face). We then cut the prism at heights \( 1.5W \) (upper surface) and \( 0.5W \) (lower surface) with two horizontal planes, and discard the shorter end pieces to produce a cube, which will represent an element of a membrane filter. The intersections of the two cutting planes and the pore throats (edges) naturally form the set of membrane inlets \( V_{\text{in}} \) and outlets \( V_{\text{out}} \), respectively (see Fig. 2 for a 2D schematic of this process, and appendix (A 1) for details).

B. Fluid Flow

We next characterize fluid flow in the membrane network. The pore throats (henceforth referred to simply as pores) are assumed to be circular cylinders. The Hagen-Poiseuille model is assumed for the flow through the pores, with validity ensured by enforcing a sufficiently small aspect ratio on the pores. The Hagen-Poiseuille equation states that fluid flux \( Q_{ij} \) is
FIG. 2: 2D schematic of the 3D network generation showing: the set of interior pore junctions $V_{\text{int}}$ (red filled circles); the pore inlets $V_{\text{in}}$ (blue filled circles) and outlets $V_{\text{out}}$ (black circles) induced by the cutting process; the cutting lines (planes in 3D), blue dotted lines; and discarded points (cyan filled circles).

Proportional to pressure difference along the pore,

$$Q_{ij} = K_{ij} (P_i - P_j), \quad K_{ij} = \frac{\pi R_{ij}^4}{8 \mu A_{ij}},$$  \hspace{1cm} (1)

$$P_i = \begin{cases} P_0, & v_i \in V_{\text{in}}, \\ 0, & v_i \in V_{\text{out}}, \end{cases}$$  \hspace{1cm} (2)

where the conductance $K_{ij}$ depends on $R_{ij}$ and $A_{ij}$, the radius and length respectively, of the pore connecting junctions $v_i$ and $v_j$. To drive the flow, we prescribe the transmembrane pressure by setting the values on the top and bottom membrane surface (per Eq. (2)), while the pressure at each interior junction is unknown. At each pore junction, we impose conservation of fluid flux, which leads to a system of equations (a discrete Laplace equation for pressure, see appendix $A2$ for details) that accounts for all connections of the network. Once the pressures at interior junctions are found, flux through each throat is determined.
C. Adsorptive Fouling

Feed solution enters the membrane top surface with a fixed foulant concentration, which serves as a boundary condition. Foulant particles are advected by the fluid while depositing on the pore walls, causing pores to shrink and eventually close up, a process known as adsorptive fouling. For each pore connecting \( v_i \) and \( v_j \) of length \( A_{ij} \), with \( Y \) a local coordinate measuring distance along a pore throat in the direction of fluid flow, let \( C_{ij}(Y,T) \) be the particle concentration at any point \( Y \) of the pore at time \( T \). The concentration satisfies the steady state advection equation

\[
Q_{ij} \frac{\partial C_{ij}}{\partial Y} = -\Lambda R_{ij} C_{ij}, \quad 0 \leq Y \leq A_{ij},
\]

(3)

\[
C_{ij}(0,T) = C_i(T),
\]

(4)

\[
C_i(T) = C_0, \quad \forall v_i \in \mathcal{V}_{in},
\]

(5)

where \( \Lambda \) is a parameter that captures the affinity between foulant particles and membrane material.

At pore junctions, assuming that fouling is negligible there, we impose conservation of foulant particle flux; that is, the total combined incoming particle flux from upstream pores must be equal to that entering downstream pores. Similar to the fluid flux conservation, this law can be expressed by a system of equations (now an advection network Laplace equation, see appendix (A 2) and Gu et al. [6] for more details) that accounts for the network connectivity.

Lastly, as foulant particles deposit on the pore wall, pore radius is assumed to decrease at a rate depending on the local foulant concentration at the pore inlet, \( C_i(t) \),

\[
\frac{dR_{ij}}{dT} = -\Lambda C_i, \quad R_{ij}(0) = R_{ij,0}.
\]

(6)

This pore evolution equation closes the model for fluid flow and foulant transport during a membrane filtration process. The filter lifetime is reached when the outgoing flux at the membrane’s downstream surface falls to zero.
### TABLE I: Key nomenclature used throughout this work.

| Dimensional Quantity | Symbol |
|----------------------|--------|
| Membrane unit length  | $W$    |
| Pressure at junction i | $P_i$ |
| Pore length          | $A_{ij}$ |
| Maximum pore length  | $D$    |
| Minimum pore length  | $D_{\text{min}}$ |
| Pore radius           | $R_{ij}$ |
| Deposition Coefficient | $\Lambda$ |
| Fluid viscosity       | $\mu$ |
| Noise amplitude       | $\beta$ |

D. Scales

The scalings for the fluid flow and foulant transport model described in the previous sections are as follows:

\[ P_i = P_0 p_i, \quad A_{ij} = W a_{ij}, \]
\[ (D, D_{\text{min}}) = W (d, d_{\text{min}}), \quad (R_{ij}, R_{ij,0}) = D_{\text{min}} (r_{ij}, r_{ij,0}), \]
\[ \lambda = \frac{8 \mu W^2}{\pi D_{\text{min}}^3 P_0} \Lambda, \quad T = \frac{D_{\text{min}}}{\Lambda C_0} t, \]

where the upper case symbols are dimensional quantities, listed in Table I.

E. Performance metrics

We evaluate the performance of a membrane network using the following two metrics: 1) total throughput ($H$) and 2) accumulated foulant concentration at membrane outlet ($C$). Total throughput is the total volume of filtrate collected at the membrane outlet over the lifetime of the membrane network filter. Accumulated foulant concentration measures the aggregate concentration of foulant particles in the collected filtrate when the filter is exhausted. Precise definitions of these quantities are given in Appendix A3.
III. INVESTIGATION METHODS

We study pore size variations by employing a random initial condition for the pore radius $r_{ij,0}$ (see Eq. (6)). More precisely, we consider perturbations to the case in which all (initial) pore radii take the same value $r_0$ by imposing a multiplicative noise,

$$r_{ij,0} = r_0 (1 + \epsilon_{ij}),$$  \hspace{1cm} (8)

where $\epsilon_{ij} \sim \text{Unif}(-\beta,\beta)$ is a uniform random variable with noise amplitude $0 < \beta < 1$, independent for each pore. For the rest of this work, when we use the terms *perturbation* or *perturb*, we are referring to Eq. (8).

We express an arbitrary model output of interest, $F$, in terms of the parameters it depends on, but primarily the noise amplitude $\beta$. We write

$$F^\beta := F(\beta, N_{total}, r_0),$$

where $F^\beta$ represents a given physical or geometric quantity under noise amplitude $\beta$. Specifically, in this work $F$ will be one of the following:

- $H$, total throughput (throughput),
- $C$, accumulated foulant concentration at membrane outlet (concentration),
- $V$, initial network porosity (porosity),
- $\tau$, initial network tortuosity (tortuosity),

where the abridged terms in parentheses are used freely henceforth. $F^0$ is then an output for a network where all pores initially have the same radius $r_0$ (no noise perturbation). We also point out that since the nondimensional model operates in the domain of a unit cube, initial void volume and membrane porosity are equal in value. We refer to *porosity* only henceon.

A principal aim of this work is to compare the influence of two independent sources of randomness, namely, the random network generation process that produces structural variations in the membrane filter (*network variability* henceforth), and the random initial condition for the pore radius that yields pore size variations (*noise variability* henceforth), on statistics of membrane filter performance metrics. Here we describe the methodology of
our study, before summarizing the approach as an algorithm with enumerated steps below. First, we generate a large number, \(N_G\), of random membrane networks (per § II A), each with the same initial pore radius \(r_0\) (see step 1 of the algorithm). We perturb the pore networks via Eq. (8) (step 2) in the following two distinct ways: To probe noise variability (step 2a), we fix one particular “typical” network, perturb it independently \(N\) times (for \(N\) sufficiently large), solve the governing equations Eqs. (1), (3) and (6) and collect statistics of performance metrics from these \(N\) realisations of noise. To probe network variability (step 2b), we perturb each of the \(N_G\) networks independently just once, and collect performance statistics from the perturbed networks.

Perturbing the radii of pore throats inevitably changes the porosity of the network, which was shown to influence strongly both of our membrane performance metrics in the unperturbed case [6]. To investigate the importance of such induced porosity changes, we devise the following strategy. First, note that initial porosity of a network is given by

\[
V = \pi \sum_{ij} r_{ij,0}^2 a_{ij},
\]

where \(a_{ij}\) is the length of a pore. For each perturbed network, we obtain its porosity via Eq. (9). We then impose this porosity on the underlying unperturbed network by determining a new initial pore radius (the same for all pore throats) such that the unperturbed and perturbed networks have the same porosity. This new unperturbed network, having the same porosity as its perturbed counterpart, is referred to as a porosity-corrected network, from which we also collect performance statistics. With these preparations, we form a score (see step 4 of the algorithm for details) that computes the difference between the outputs of the perturbed and porosity-corrected networks, and normalizes by the output of the underlying unperturbed network.

We summarize the above procedures in the following algorithm. To distinguish clearly the two sources of randomness (random network generation and noise perturbation), we introduce additional subscript notation, using double indices \(i\) and \(j\) to label the network and noise realisation (respectively). We also label a fixed network with subscript \(i_0\). All geometric parameters and indices used in the algorithm are listed in Table II.

Each of the \(N_G\) membrane networks has a fixed maximum pore length \(d = 0.3\), minimum pore length \(d_{\text{min}} = 0.06\) and initial unperturbed pore radius \(r_0 = 0.01\). We vary two parameters: 1) noise amplitude \(\beta\); and 2) total number of pore junctions \(N_{\text{total}}\) (the range of
| Parameter                              | Symbol | Values         |
|----------------------------------------|--------|----------------|
| Initial number of pore junctions       | $N_{\text{total}}$ | 500, 775       |
| Maximum pore length                    | $d$    | 0.3            |
| Minimum pore length                    | $d_{\text{min}}$ | 0.06           |
| Initial unperturbed pore radius        | $r_0$  | 0.01           |
| Noise Amplitude                        | $\beta$ | 0.06, 0.25, 0.5, 0.7 |
| Number of networks                     | $N_G$  | 1000           |
| Network index                          | $i$    | $[1, N_G]$     |
| Number of noise realisations           | $N$    | 500            |
| Noise realisation index                | $j$    | $[1, N]$       |

TABLE II: Key parameters used in simulations

values of each is listed in Table II. The ensuing study first fixes a porosity regime by fixing $N_{\text{total}}$ while varying $\beta$. Though $r_0$ is held fixed, we retain it in the following expressions to distinguish the porosity-corrected networks from others. The algorithm at the heart of our study is the following:

1. (Random network generation) Choose $N_{\text{total}}$. Generate $N_G$ unperturbed networks,

$$G^0_i := G_i (0, N_{\text{total}}, r_0), \quad i = 1, \ldots, N_G.$$  

Compute model outputs $F^0_i$ as a base case for the network $G^0_i$.

2. (Noise perturbation) Choose noise amplitude $\beta$. Let $G^\beta_{ij}$ represent network $i$ under perturbation realisation $j$.

   (a) (noise variability) Fix a typical network $G^0_{i0}$, perturb $N$ times independently and obtain

   $$G^\beta_{i0j}, \quad j = 1, \ldots, N.$$  

   Compute $F^\beta_{i0j}$, referred to as output under noise realisations.

   (b) (network variability) Perturb each $G^0_i$ once independently via Eq. (8) and obtain

   $$G^\beta_{ii1}, \quad i = 1, \ldots, N_G.$$
Compute $F_{ii_1}^\beta$, referred to as output under network realisations. The second subscript $i_1$ is chosen to indicate that though the noise perturbation for each network is realised once, the realisation will be different from network to network (hence the $i$ dependence).

3. (Porosity correction) For each network $G_{ij}^\beta$ of porosity $V_{ij}^\beta$, consider an unperturbed $G_{ij,*}^0 (0, N_{\text{total}}, r_{0}^*)$ such that its porosity $V_{ij,*}^0 = V_{ij}^\beta$. We find that

$$r_{0}^* = \sqrt{\frac{V_{ij}^\beta}{V_{i}^0 r_{0}^*}},$$

where $V_{i}^0$ is the porosity of the $i$-th unperturbed network (see Appendix A5 for a short derivation). Compute outputs $F_{ij,*}$ for the porosity-corrected networks.

4. (Scores) We construct two scores that characterize the network and noise variability when comparing networks of equal porosity.

   (a) (Noise score) Fix a network $G_{i_0}^0$ with output $F_{i_0}^0$. For the noise realisations $G_{i_0,j}^\beta$ on this network obtained in step 2a, we compute the following score

$$\hat{F}_{i_0,j}^\beta = \frac{F_{i_0,j}^\beta - F_{i_0,j,*}^0}{F_{i_0}^0}, \quad j = 1, \ldots, N,$$

where $F_{i_0,j,*}^0$ is computed for the porosity-corrected network found in step 3.

   (b) (Network score) Perform step 2b to obtain $G_{ii_1}^\beta$ and compute output $F_{ii_1}^\beta$. Compute the score for each network,

$$\hat{F}_{i,i_1}^\beta = \frac{F_{i,i_1}^\beta - F_{i,i_1,*}^0}{F_{i}^0}, \quad i = 1, \ldots, N_G,$$

where $F_{i,i_1,*}^0$ is computed for the porosity-corrected network found in step 3 (by setting $j = 1$).

In all discussions below, we refer to the quantities defined by Eq. (11) or (12) as porosity-corrected scores.

5. Obtain the means of model outputs $\overline{F}^\beta$ and normalized scores $\overline{\hat{F}}^\beta$. The mean under noise and network realisations is computed by averaging over the number of noise and network realisations respectively.

6. Go back to step 2 with a different $\beta$.

7. Go back to step 1 with a different $N_{\text{total}}$ (to vary initial porosity).
IV. RESULTS AND DISCUSSIONS

In § IV A, we study the performance metrics under a specific choice of model parameters as an example. In § IV B, we reinforce the example by a thorough sweep of the parameter space with our main results.

A. Example: Low Noise Regime $\beta = 0.06$ and Low Porosity $V \approx 0.25$

In this section, we present a set of results for membrane pore networks in the regime of low noise amplitude perturbations and low initial porosity. We specifically choose this parameter regime as an example because the results at higher porosities are in fact qualitatively similar (shown in the next section) but more time-consuming to compute. More precisely, we fix noise amplitude $\beta = 0.06$ and generate $N_G = 1000$ networks with an initial number of points $N_{\text{total}} = 500$, which yield an ensemble average initial porosity $V \approx 0.25$ (averaged over $N_G$ unperturbed networks). When we study noise variability (per step 2(a) in the algorithm), we fix a typical network with initial porosity very close to the ensemble average, 0.25 within this particular section. We will first compare the statistics of performance metrics (per steps 4a and 4b in the algorithm) and then discuss the similarities and differences in the network and noise scores in terms of the initial porosity and tortuosity of the networks, similarly averaged over many network and noise realizations.

1. Throughput and Porosity

Fig. 3 shows throughput vs porosity under (a) noise and (b) network realizations, respectively. Note the different scales in the two figures: in Fig. 3b, we also plot a black rectangle that represents the total range of Fig. 3a, showing that network variability dominates noise variability in this noise/porosity regime. That is, for the present case, structural network variations incur much more variance in total throughput than pore size variations.

As noted above, and as evident from Fig. 3, each pore size perturbation leads to a porosity variation. Since initial porosity is known to be a strong parameter that effectively determines total throughput (per Gu et al. [6]), it is natural to ask if the induced initial porosity change is primarily responsible for the difference in membrane performance under pore size variations. We address this question using the noise and network scores, formulated in Eqs. (11) and (12).
FIG. 3: Scatter plot for throughput vs porosity (a) $\left\{H_{\nu j}^{\beta}\right\}_{j=1}^{N}$ under $N = 500$ noise realisations and (b) $\left\{H_{11}^{\beta}\right\}_{j=1}^{N_G}$ under $N_G = 1000$ network realizations (with each network perturbed once), with the range of the scatter plot in (a) denoted by a black rectangle. For all plots, $d = 0.3$, $N_{\text{total}} = 500$ and $\beta = 0.06$.

in step 4 of the algorithm in §3. Recall that throughput score characterizes the difference in throughput between a perturbed network (pore sizes varied) and an unperturbed one of equal porosity. In Fig. 4, we present histograms of throughput scores under noise and network realizations. We see that the two histograms have very similar distributions. Comparing figures 3 and 4, we deduce that the porosity change is the crucial factor since Fig. 4, in marked contrast to Fig. 3, shows variations of network and noise to have a very similar effect.

2. Concentration and Tortuosity

We next investigate the influence of noise perturbation on the accumulated concentration of particle impurities in the filtrate (concentration) and the tortuosity of the pore network, quantities that are strongly related in unperturbed pore networks [6]. First, Fig. 5 shows concentration vs tortuosity under (a) noise and (b) network realizations. In Fig. 5b, a black rectangle shows the total range of Fig. 5a, showing that the ranges of both concentration and
FIG. 4: Histogram for throughput score for (a) \( \{ \hat{H}_\beta \}^N \) under \( N = 500 \) noise realisations (b) \( \{ \hat{H}_{11} \}^{N_G} \) under \( N_G = 1000 \) network realizations (with each network perturbed once). Same parameters as Fig. 3.

tortuosity under different noise realisations in Fig. 5a are far smaller than their counterparts under different network realisations. This again implies that network variability overwhelms noise variability in the present case.

In figures 6a and 6b, we plot the tortuosity data of figure 5 as a histogram of tortuosity under noise and network realizations (respectively). Note the different horizontal ranges on the two plots (cf. figure 5): tortuosity under noise realisations has a far smaller range than under graph realisations, again illustrating how network variability dominates noise variability. Furthermore, in Fig. 6b, we see that the distribution of tortuosity shifts slightly to the right relative to the unperturbed case, suggesting that noise perturbation increases initial tortuosity. We speculate that this could be because a positive noise amplitude on average increases porosity, in particular, the volume of the inlets, which, in turn, increases the initial flux level at the membrane inlets and thus tortuosity (see \( \pi_0 \) term in Eq. (A11) in appendix A 4).

In Fig. 7, we show histograms for the porosity-corrected concentration and tortuosity scores under noise (Figs. 7a, 7c, generated using Eq. (11)) and network (Figs. 7b, 7d, generated using Eq. (12)) realizations. We find that the histograms of concentration scores
FIG. 5: (a)-(b) Same description and parameters as in Fig. 3 for concentration $C$ and tortuosity $\tau$.

FIG. 6: Histogram of tortuosity under (a) noise realisations and (b) network realisations. Same parameters as in Fig. 3.

in Fig. 7a and 7b are very similar in shape and width, suggesting that, after we correct for porosity differences, perturbing a network many times is equivalent to perturbing many networks once. This phenomenon further emphasises the importance of porosity as a critical geometric feature of the network that decides membrane performance. Similarly, the
histograms of tortuosity scores in Fig. 7c and 7d under noise and network realizations (respectively) share very similar distributions, indicating that tortuosities of porosity-corrected membrane networks are affected similarly to those of the uncorrected counterparts by pore size variations.

FIG. 7: Same description and parameters as Fig. 4 for (a)-(b) concentration score $\hat{C}$ and (c)-(d) tortuosity score $\hat{\tau}$. Noise scores are in blue and network scores are in red.
B. Results for higher porosity $V$ and noise amplitude $\beta$

We now explore the influence of larger noise amplitude $\beta$ and larger network porosity $V$. For brevity, we condense results (in Figs. 8a, 9a and 10) for different initial porosity regimes in terms of the average outputs and their standard deviations (shown via error bars) plotted as a function of noise amplitude. From the results in §IV A, with modest noise amplitude, $\beta = 0.06$, the noise variability has a rather insignificant effect on both chosen measures of performance (throughput and concentration) compared to network variability. We now probe the consistency of this finding in other parameter regimes.

In Fig. 8a and 8b, we plot the mean throughput $\overline{H}^\beta$ against noise amplitude $\beta$ for low and high network porosity regimes respectively, with the error bars representing the standard deviation of each statistic. We see that the error bars for network variability (in red) are much larger than those for noise variability, for any value of noise amplitude $\beta$, in both porosity regimes. However, when we plot the mean throughput scores $\hat{H}^\beta$ (which correct for porosity changes in perturbed networks), shown in Figs. 8c and 8d via the same setup, the error bars under noise and network realisations have much greater overlap, in both porosity regimes, for all $\beta$ values considered. This again underscores the importance of network porosity, which appears to account for the difference between network and noise variability seen in Fig. 8a and 8b.

In Fig. 9a and 9b, we present mean concentration $\overline{C}^\beta$ as a function of noise amplitude $\beta$ for low and high porosity regimes. We notice a similar trend as for mean throughput (Fig. 8a and 8b): network variability dominates noise variability for all porosities and noise amplitudes tested. However, the dominance is much less severe for particle concentration than for throughput: we note that in Fig. 9a, the size of the blue error bars under noise realisations relative to the red ones under network realisations, is much larger than in Fig. 8a. This means that concentration, as a performance metric, experiences larger variations from noise perturbation than does throughput.

In Fig. 9c and 9d, we plot the mean concentration scores $\hat{C}^\beta$ (see Eqs. (11) and (12)), which correct for porosity variations, against noise amplitude $\beta$. We see that the error bars of both noise and network realisations overlap to a greater degree than the results in Fig. 9a and 9b. This shows that the porosity variation caused by noise perturbation plays an important role in membrane performance, regardless of noise amplitude and initial porosity. However,
FIG. 8: Mean and mean score, respectively, of throughput $\overline{H^\beta}$ vs. noise amplitude $\beta$ for (a)(c) low porosity $V \approx 0.25$ and (b)(d) high porosity $V \approx 0.6$. Vertical error bars are standard deviations for each mean value.

the consistency of the extent of overlap is not maintained for all parameter regimes. In particular, we find that while the overlap is strong for low noise amplitude in both porosity regimes (see the first two data points from the left in Fig. 9c and 9d), the overlap at high noise amplitudes is relatively smaller in the low porosity regime than the high one.

In Fig. 10 we plot mean tortuosity and mean tortuosity scores against noise amplitude for both low and high porosity regimes. In Figs. 10a and 10b we plot mean tortuosity $\overline{\tau^\beta}$
FIG. 9: Same setup as in Fig. 8, here for mean concentration $\overline{C^\beta}$ and concentration score $\hat{C}^\beta$ against noise amplitude $\beta$ for low and high porosity networks respectively. We find that in both porosity regimes, network variability still dominates noise variability (less strongly for higher noise amplitudes). By looking at the sizes of the blue error bars (noise variability) relative to the red ones (network variability), we see that for large noise amplitudes, the sizes become similar. This indicates that sufficiently high noise amplitude induces similar variability in network tortuosity to that due to the network generation protocol.

In Fig. 10c and 10d, we plot mean tortuosity score $\overline{\tau^\beta}$ for both low and high porosity
regimes. We observe that noise and network variability now are very similar for all noise amplitudes considered, in both porosity regimes. This further reinforces our earlier findings from throughput and concentration that porosity is a critical feature of the network.

FIG. 10: Same setup as in Fig. 8 here for mean tortuosity $\overline{\tau_\beta}$ and tortuosity score $\overline{\hat{\tau}}_\beta$.

V. CONCLUSIONS

In this work, we have described and implemented a network model for the pore structure of a membrane filter by randomly generating pore junctions and throats according to a well-
defined protocol. Within this network model, we have modelled pore size variations within a membrane filter as random initial conditions (noise) for the pore radii and examined their effects on two key membrane filter performance metrics: total throughput and accumulated concentration of adsorptive foulants. From this study, we have found that the variability of the chosen performance metrics incurred by the random network generation procedure, dominates that due to the noise. This suggests that, though pore size variations do matter for analysis on a single network, they are incomparable to the influence of the variance of a large ensemble of membrane filter networks. Furthermore, by considering porosity-corrected scores of the performance metrics, we conclude that the initial porosity of the pore network is a critical geometric feature of the filter, and a strong determinant of performance. For future work, we plan to consider other fouling mechanisms such as large-particle sieving in addition to adsorption, and investigate the effect of pore size variations within the more general setting.

ACKNOWLEDGMENTS

This work was supported by NSF Grant No. DMS-1615719.

Appendix A: Model details

1. Network Generation

We generate a membrane pore network via a variant of the Random Geometric network (RGG). To generate the set of pore junctions \( \mathcal{V} \), we place \( N_{\text{total}} \) randomly distributed points (following a uniform distribution) in a rectangular box with square cross-section of side length \( W \) and height \( 2W \). We connect points that lie within a distance of \( D \), but also at least \( D_{\text{min}} \) apart, the latter a control parameter such that when chosen large enough relative to the pore radius, it ensures validity of the Hagen-Poiseuille framework used to model fluid flow. These connections form a set of pore throats \( \mathcal{E} \) and together with the set of pore junctions \( \mathcal{V} \) we obtain an initial network \( G = G (\mathcal{V}, \mathcal{E}) \). We say \( (v_i, v_j) \in \mathcal{E} \) when two pore junctions \( v_i, v_j \in \mathcal{V} \) form a pore throat.

We then cut through the rectangular box with two horizontal planes at heights \( 0.5W \) and \( 1.5W \), respectively. The intersections of these two planes and the set of pore throats \( \mathcal{E} \) form
the set of inlets $\mathcal{V}_{\text{in}}$ and outlets $\mathcal{V}_{\text{out}}$ respectively. Altogether, the above procedure forms the domain for fluid flow and fouling, described in §2.3.

2. The graph Laplacian

We associate each network $G$ with a (weighted) graph Laplacian that describes the connection strength between pore junctions,

$$L_W := D - W,$$  \hspace{1cm} (A1)

where $D$ is the (diagonal) $W$-weighted degree matrix with entries

$$D_{ij} = \begin{cases} \sum_{k=1}^{\vert V \vert} W_{ik}, & j = i, \\ 0, & \text{otherwise}, \end{cases}$$  \hspace{1cm} (A2)

and $W$ is a weighted adjacency matrix, with nonnegative entries $W_{ij}$ when $(v_i, v_j) \in E$, to be specified according to context. We also say that $e_{ij}$ is a pore throat connecting $v_i$ and $v_j$ iff $W_{ij} > 0$ (or simply, $v_i$ and $v_j$ are connected or adjacent).

While the above setup characterizes the flux inside an individual pore throat, we employ conservation of flux at each vertex $v_i$ throughout the network,

$$0 = \sum_{v_j : (v_i, v_j) \in E} q_{ij}.$$  \hspace{1cm} (A3)

Combining Eqs. (1) and (A3), we form a discrete Laplace equation for pressure $P$ at each vertex,

$$L_k p(v_i) = 0, \quad v_i \in \mathcal{V}_{\text{int}},$$  \hspace{1cm} (A4)

$$p(v) = p_0, \quad v \in \mathcal{V}_{\text{in}},$$  \hspace{1cm} (A5)

$$p(v) = 0, \quad v \in \mathcal{V}_{\text{out}},$$  \hspace{1cm} (A6)

where $L_k$ is the graph Laplacian of $G$ weighted by conductance $k$. Once the pressures $p(v_i)$ are found for all interior pore junctions $v_i \in \mathcal{V}_{\text{int}}$, we use Eqs. (1) to find flux $q_{ij}$ in each pore throat to form a flux matrix $q$ with $i$ and $j$ as row and column indices respectively.

Using conservation of particle flux at each junction, we arrive at the following advection
Laplace equation for foulant concentration $c_i(t)$ at each vertex $v_i \in V \setminus V_{in}$,

$$L_{q}^{\text{in}}c = (q \circ b)^T c_0,$$  \hspace{1cm} (A7)

$$c_0 = (1, \ldots, 1, 0, \ldots, 0)^T, \quad b_{ij} = \exp \left( -\frac{\lambda r_{ij} a_{ij}}{q_{ij}} \right),$$  \hspace{1cm} (A8)

where $L_{q}^{\text{in}} = D_q^T - (q \circ b)^T$ is called *advection Laplacian* with a sink $b$. $\circ$ and $\cdot$ denote matrix transpose and the element-wise multiplication respectively. See Gu et al. [6] for a detailed derivation of this linear system.

### 3. Performance metrics

Volumetric throughput of a membrane filter over its operational lifetime is a commonly-used measure of overall efficiency. The volumetric throughput $H(T)$ through the filter is defined by

$$H(T) = \int_0^T Q_{\text{out}}(T') \, dT', \quad (A9)$$

$$Q_{\text{out}}(T) = \sum_{v_j \in V_{\text{out}}} \sum_{v_i: (v_i, v_j) \in E} Q_{ij}(T), \quad (A10)$$

where $Q_{\text{out}}(T)$ is the total flux exiting the filter. In particular, we are interested in $H_{\text{final}} := H(T_{\text{final}})$, the total volume of filtrate processed by the filter over its lifetime.

Another performance measure is the accumulated foulant concentration in the filtrate, which captures the aggregate particle capture efficiency of the filter. The accumulated foulant concentration is defined by

$$C_{\text{acm}}(T) = \frac{\int_0^T C_{\text{out}}(T') Q_{\text{out}}(T') \, dT'}{\int_0^T Q_{\text{out}}(T') \, dT'},$$

where

$$C_{\text{out}}(T) = \frac{\sum_{v_j \in V_{\text{out}}} \sum_{v_i: (v_i, v_j) \in E} C_j(T) Q_{ij}(T)}{Q_{\text{out}}(T)}.$$ 

Of particular interest is $C_{\text{final}} := C_{\text{acm}}(T_{\text{final}})$, which provides a measure of the aggregate particle capture efficiency of the filter over its lifetime.
4. Tortuosity

Tortuosity of a membrane network $\tau$ is defined by the average distance travelled by a fluid particle from membrane top surface to bottom, relative to membrane thickness $W$. We here provide a formula via a probabilistic approach,

$$\tau = \frac{\pi T}{W} \left( \sum_{n=1}^{m} P^{n-1} \right) \text{diag} (PW_E),$$  \hspace{1cm} (A11)

where $T$ means vector transpose and diag means the diagonal component of a matrix. Here we provide some intuition for each term. The initial distribution $\pi_0$ describes the probability of the fluid particle choosing an inlet on the membrane top surface. To calculate $\pi_0$, we compute the proportion of flux entering each inlet on the upstream surface relative to total flux. $P$ within the sum describes the law of how a fluid particle traverses the network from one junction to its adjacent neighbors (known as a step); the upper limit $m$ is the largest number of steps a particle takes to exit the membrane bottom surface, which can be found for each network. Lastly, diag $(PW_E)$ describes the average distance travelled by the fluid particle in one step starting from each junction. We refer the reader to Gu et al. [6] for details of the derivation.

5. Porosity correction

Per Eq. (10) in item 3 (porosity correction) of the algorithm, we here derive the expression for $r^*_{0}$, the unknown radius of an unperturbed network (same for all pore throats) such that its porosity $V^{0}_{ij,*}$ is equal to the known perturbed network $V^{\beta}_{ij}$. It relies on writing $V^{0}_{ij,*}$ in terms of $V^{0}$, the porosity of the unperturbed network with initial radius $r_0$:

$$V^{\beta}_{ij} = V^{0}_{ij,*} = \pi \left( r^*_0 \right)^2 \sum_{\text{edge}} \text{(edge length)}$$

$$= \pi r_0^2 \sum_{\text{edge}} \text{(edge length)} \left( \frac{r^*_0}{r_0} \right)^2$$

$$= V^{0} \left( \frac{r^*_0}{r_0} \right)^2$$

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and thus $r_0^* = \sqrt{\frac{V_0}{V_0}} r_0$. 

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