

# Mean survival times of absorbing triply periodic minimal surfaces

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Understanding the transport properties of a porous medium from a knowledge of its microstructure is a problem of great interest in the physical, chemical, and biological sciences. Using a first-passage time method, we compute the mean survival time  $\tau$  of a Brownian particle among perfectly absorbing traps for a wide class of triply periodic porous media, including minimal surfaces. We find that the porous medium with an interface that is the Schwartz  $P$  minimal surface maximizes the mean survival time among this class. This adds to the growing evidence of the multifunctional optimality of this bicontinuous porous medium. We conjecture that the mean survival time (like the fluid permeability) is maximized for triply periodic porous media with a simply connected pore space at porosity  $\phi=1/2$  by the structure that globally optimizes the specific surface. We also compute pore-size statistics of the model microstructures in order to ascertain the validity of a “universal curve” for the mean survival time for these porous media. This represents the first nontrivial statistical characterization of triply periodic minimal surfaces.

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## I. INTRODUCTION

Fluid-saturated porous media are ubiquitous in nature (e.g., geological and biological media) and in synthetic situations (e.g., filters, cements, and foams) [1,2]. Understanding the transport properties of a porous medium from a knowledge of its microstructure is a subject that spans many fields [1–6]. In particular, physical phenomena involving simultaneous diffusion and reaction in porous media abound in the physical and biological sciences [1,2,7]. Considerable attention has been devoted to instances in which diffusion occurs in the pore region of the porous medium with a “trap” region whose interface can absorb the diffusing species via a surface reaction. Examples are found in widely different processes, such as heterogeneous catalysis, fluorescence quenching, cell metabolism, ligand binding in proteins, migration of atoms and defects in solids, and crystal growth [1]. A key parameter in such processes is the *mean survival time*  $\tau$ , which gives the average lifetime of the diffusing species before it gets trapped.

It is noteworthy that while there has been a significant amount of progress made on the determination of the structures that optimize a variety of transport and mechanical properties of porous media [1,8,9], there have been no studies that have attempted to find the optimal isotropic structures for the mean survival time  $\tau$  [10]. It has been recently demonstrated that triply periodic two-phase bicontinuous composites with interfaces that are the Schwartz  $P$  and  $D$  minimal surfaces are not only geometrically extremal but are also extremal for simultaneous transport of heat and electricity [11–13]. A minimal surface is one that is locally area minimizing, i.e., every point has zero mean curvature. Triply

periodic minimal surfaces are minimal surfaces that are periodic in all three coordinate directions. An important subclass of triply periodic minimal surfaces are those that partition space into two disjoint but intertwining regions that are simultaneously continuous (i.e., bicontinuous) [14,15]. Examples of such surfaces include the Schwartz primitive ( $P$ ), the Schwartz diamond ( $D$ ), and the Schoen gyroid ( $G$ ) surfaces (see Fig. 1); each disjoint region has a volume fraction equal to 1/2. Such triply periodic minimal surfaces arise in a variety of systems, including nanocomposites [17], micellar materials [18], block copolymers [19], as well as lipid-water systems and certain cell membranes [20–23].

The multifunctionality of such two-phase systems has been further established by showing that they are also extremal when a competition is set up between the effective bulk modulus and electrical (or thermal) conductivity of the bicontinuous composite [24]. Jung and Torquato [16] also explored the multifunctionality of the three minimal surfaces shown in Fig. 1 with respect to Stokes (slow viscous) flow. The simulations conducted by Jung and Torquato revealed that the Schwartz  $P$  porous medium has the largest fluid permeability  $k$  among a class of structures studied with porosity  $\phi=1/2$ . Further, the fluid permeability was found to be inversely proportional to the specific surface  $s$  (interface

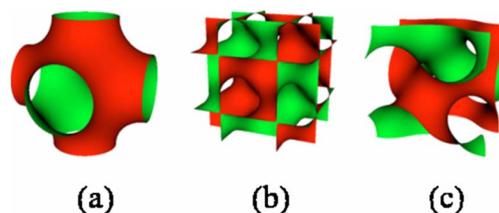


FIG. 1. (Color online) Unit cells of three different minimal surfaces. (a) Schwartz  $P$  surface, (b) Schwartz  $D$  surface, (c) Schoen  $G$  surface. Image is adapted from Ref. [16].

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area per unit volume). This led the authors to conjecture that the maximal fluid permeability for a triply periodic porous medium with a simply connected pore space [25] at a porosity  $\phi=1/2$  is achieved by the structure that globally minimizes the specific surface [16].

In this paper, we explore whether the mean survival time  $\tau$  of a Brownian particle among perfectly absorbing traps is maximized by the Schwartz  $P$  structure among a wide class of triply periodic porous media based on the class of six models studied in Ref. [16]. Further, we go beyond considering just a representative medium from each class of models and explore several of the models over a *range* of parameter values, as will be further explained below. This inquiry is also motivated by a cross-property bound that rigorously links the fluid permeability  $k$  to the mean survival time  $\tau$  [26],

$$k \leq \tau. \quad (1)$$

It should be noted that the inequality of Eq. (1) becomes an equality for transport in parallel cylindrical tube bundles of arbitrary cross-sectional geometry [26,27]. It is also a relatively tight bound (when appropriately scaled) for transport around distributions of inclusions [26]. It is clear that the permeability  $k$  will be maximized for a simply connected pore space (e.g., the presence of dead ends is undesirable because they would not contribute to the flow). Inequality (1) and the results of Ref. [16] suggest that  $\tau$  is maximized by the same simply connected microstructure that maximizes  $k$  for  $\phi=1/2$ .

We will also test whether our calculations for  $\tau$  collapse on to a “universal” scaling relation for the mean survival time [28]. This requires us to compute the pore-size density functions for the triply periodic surfaces considered in this paper.

In Sec. II, we define terminologies and give a precise statement of the problem. In Sec. III, we describe the first-passage time technique that we utilize to compute the mean survival time for a wide class of triply periodic porous media that are generally bicontinuous. Section IV reports our finding for  $\tau$ . In Sec. V, we discuss a universal scaling relation for  $\tau$ , report pore-size statistics for the triply periodic porous media studied here, and ascertain the applicability of the universal curve for these structures. Finally, in Sec. VI, we make concluding remarks and discuss the ramifications of our results.

## II. DEFINITIONS AND PROBLEM STATEMENT

The mean survival time  $\tau$  arises in steady-state diffusion of reactants in a trap-free pore region  $\mathcal{V}_1$  with diffusion coefficient  $D$  among static traps with a unit rate of production of the reactants per unit pore volume [1]. When the reactants come in contact with the pore-trap interface  $\partial\mathcal{V}$ , they get absorbed. Using homogenization theory [1], it has been shown that  $\tau$ , the average time traveled before a diffusing particle gets trapped, is given by

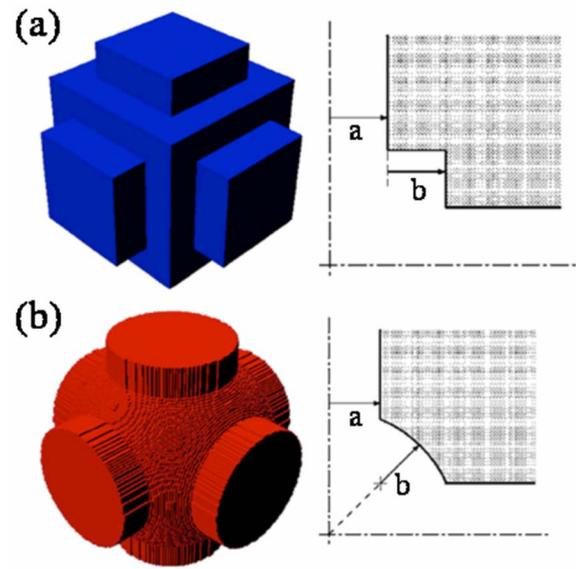


FIG. 2. (Color online) Unit cells of two different pore-channel models. (a) Cubic pore-square channel and its cross section. (b) Spherical pore-circular channel and its cross section. Image is adapted from Ref. [16].

$$\tau = \frac{\langle u \rangle}{\phi D}, \quad (2)$$

where  $u(\mathbf{r})$  is the scaled concentration field of reactants, which satisfies the diffusion equation

$$\Delta u = -1 \quad \text{in } \mathcal{V}_1, \quad (3)$$

$$u = 0 \quad \text{on } \partial\mathcal{V}, \quad (4)$$

and  $\Delta$  is the Laplacian operator.

Following Ref. [16], we compute  $\tau$  for a wide class triply periodic structures: the Schwartz  $P$ , Schwartz  $D$ , and Schoen  $G$  minimal surfaces (Fig. 1), a cubic pore-square channel model [Fig. 2(a)], and a spherical pore-circular channel model [Fig. 2(b)], and an array of spherical traps arranged on a simple-cubic lattice [29] (which of course is not bicontinuous). The pore-channel models each contain two parameters,  $a$  and  $b$ , that enable one to control the relative size of the pores (either spherical or cubic in shape) to the size of the channels (either circular or square cross sections) [16]. The parameter  $a$  determines channel width/diameter, whereas  $b$  determines the width/diameter of the pore. This class of models is bicontinuous provided that  $a > 0$ . In the current investigation, we compute  $\tau$  for the pore-channel models using a wider range of values for  $a$  and  $b$  than used in Ref. [16], while keeping  $\phi$  fixed at  $1/2$ .

## III. FIRST-PASSAGE TIME METHOD FOR COMPUTING MEAN SURVIVAL TIME

The mean survival time  $\tau$  for the aforementioned triply periodic porous media could be calculated using standard random-walk techniques that simulate the detailed zigzag trajectory of a Brownian particle [30]. We instead compute  $\tau$

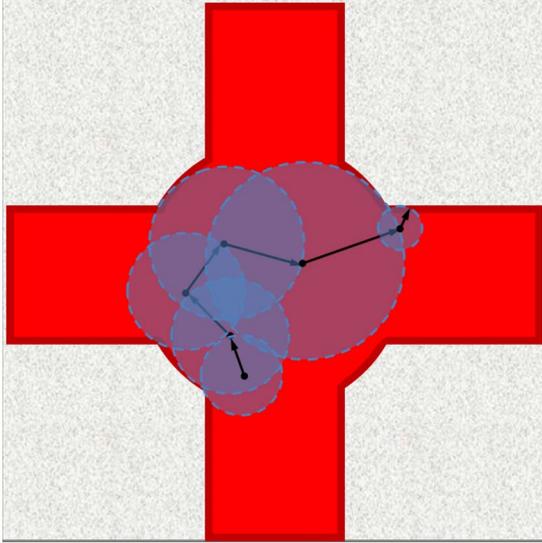


FIG. 3. (Color online) Two-dimensional depiction of continuous first-passage time method applied to the spherical pore-circular channel model. The Brownian particle walks, by jumping to the surface of the largest possible first-passage sphere at each step, until it gets trapped at the two-phase interface (maroon boundary layer, which appears as dark gray if the image is being viewed in black and white).

for these microstructures using an efficient first-passage time algorithm [31]. The fundamental periodic cell is taken to be a cube of side length unity.

The first-passage time algorithm is implemented by applying the following set of rules:

- (1) Introduce a Brownian particle into a random position in the trap-free phase.
- (2) While the walker is sufficiently far from the two-phase interface, construct the largest sphere of radius  $R_i$  centered at the Brownian particle that just touches the two-phase interface.
- (3) In one step, the walker jumps to a random point on the surface of the sphere (Fig. 3), with an average hitting time of

$$\bar{\tau} = R_i^2 / (6D). \tag{5}$$

- (4) Repeat steps (2) and (3) until the walker is within some prescribed small distance  $\delta$  (taken to be  $10^{-8}$  in our simulations) from the two-phase interface.
- (5) Repeat steps (1)–(4) for many random walkers and calculate the mean survival time from the following equation:

$$\tau = \frac{\langle \sum_i R_i^2 \rangle}{6D}, \tag{6}$$

where the angular brackets denote an ensemble average.

The mean survival time  $\tau$  of the pore-channel models are determined using this algorithm. However, since we only have discrete (not continuous) representations of the minimal surfaces [16], the discrete analog of the algorithm is utilized in these cases [32]. In the discrete case, first-passage cubes of

TABLE I. Mean survival time  $\tau$ , fluid permeability  $k$ , and specific surface  $s$  of triply periodic structures. All quantities are made dimensionless using the side length of the unit cell.

Structure	$\tau$	$k$	$s$
Schwartz $P$	0.0173950	0.0034765	2.3705
Schoen $G$	0.0093266	0.0022889	3.1284
Schwartz $D$	0.0060414	0.0014397	3.9011
Cubic-pore channel			
( $a=0.25;b=0$ )	0.0139289	0.0030744	3.0000
( $a=0.1324;b=0.25$ )	0.0123813	0.0005310	3.8360
( $a=0.0781;b=0.3125$ )	0.0122259	0.0000948	3.9254
( $a=0;b=0.3969$ )	0.0127852		3.7804
Sphere-pore channel			
( $a=0.2836;b=0$ )	0.0167934	0.0034596	2.63990
( $a=0.1480;b=0.2794$ )	0.0164995		2.73649
( $a=0.0908;b=0.3633$ )	0.0161733		2.93057
( $a=0;b=0.4924$ )	0.0161093		3.04681
Spherical trap ( $\phi=0.5$ )	0.0139640	0.0030591	3.0780

length  $2R_i$  are utilized instead of first-passage spheres, and the average time it takes to move to the surface of a first-passage cube is  $\bar{\tau} \approx 0.225R_i^2/D$ .

#### IV. RESULTS FOR THE MEAN SURVIVAL TIMES

The value of  $\tau$  for each of the aforementioned models is given in Table I, along with the fluid permeability and specific surface. All fluid permeability measurements (if available), as well as the specific surface measurements for the minimal surfaces, and the pore-channel models with  $b=0$  are taken from Ref. [16]. We see that  $\tau$  always obeys the rigorous bound specified by Eq. (1). We also see that a simply connected pore phase is a crucial topological feature required to achieve large mean survival times at a porosity  $\phi=1/2$ . However, a simply connected pore phase is not a sufficient condition, as evidenced by the relatively small mean survival times associated with the Schwartz  $D$  and Schoen  $G$  minimal surfaces. These two minimal surfaces have rather large specific surfaces and hence serve as efficient traps for the diffusing Brownian particles. Indeed, we see that the survival times are inversely proportional to the corresponding specific surfaces for all of the bicontinuous structures. The pore spaces of structures with large  $\tau$  are expected to be simply connected, and therefore it would not be unreasonable for the survival time to be inversely proportional to the specific surface in these instances. As hypothesized, we find that among the structures examined, the Schwartz  $P$  porous medium maximizes the mean survival time. To get some idea of the fluctuations about the average  $\tau$  values, we computed the associated variance  $\sigma_\tau^2$  for trapping for the three minimal surfaces and found that  $\sigma_\tau^2=0.000\ 51$ ,  $0.000\ 13$ , and  $0.000\ 05$  for the Schwartz  $P$ , Schoen  $G$ , and Schwartz  $D$  surfaces, respectively.

Given that both the mean survival time  $\tau$  and fluid permeability  $k$  are made dimensionless with the side length of the

unit cell, one might ask why these dimensionless bulk properties are 2–3 orders of magnitude smaller than unity. This is a well-known behavior for such transport properties of porous media, optimal or not [1,2]. For example, the fluid permeability (average of the velocity field) can be regarded to be the “effective pore-channel area of the dynamically connected” part of the pore space. For nonsimply connected pore spaces, there generally will be regions that contain fluid but do not actively contribute to the flow (not dynamically connected). Moreover, because of the no-slip condition, the velocity only becomes significantly large sufficiently away from the pore-solid interface for general porous media. Thus, these two effects conspire to make the effective area of a pore channel, i.e., the fluid permeability  $k$ , considerably less than the geometric pore-channel sizes. (This effect is even true for the simple case of flow in a tube; see Ref. [27].) Similar arguments apply to the mean survival time. The perfectly absorbing boundary condition at the pore-solid interface (i.e., zero concentration field) means that the concentration field becomes appreciably large sufficiently away from the pore-solid interface, which results in a mean survival time (average of the concentration field) that is generally several orders of magnitude smaller than dictated by the largest pore dimensions.

**V. PORE-SIZE FUNCTIONS AND UNIVERSAL SCALING RELATION FOR SURVIVAL TIME**

**A. Pore-size function**

Porous media whose interfaces are triply periodic minimal surfaces apparently have remarkable macroscopic properties. Nonetheless, these structures have yet to be statistically characterized using nontrivial descriptors. Here we present pore-size functions for these structures as well as the triply periodic circular channels. This is motivated by the fact that the pore-size density function  $P(\delta)$  arises in rigorous lower bounds on  $\tau$  [1] as well as a universal curve for  $\tau$  [28] described below. The quantity  $P(\delta)d\delta$  gives the probability that a randomly chosen point in the pore region lies at

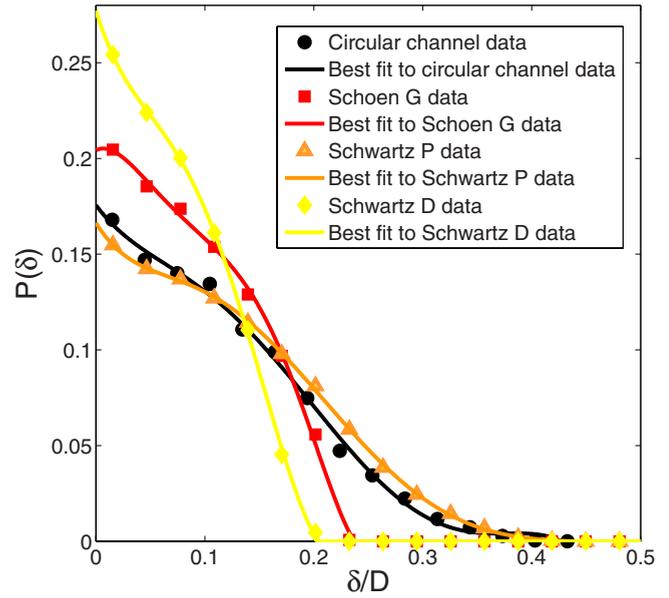


FIG. 4. (Color online) Pore-size density function data generated from the presented algorithm for the three minimal surfaces and the circular-channel model along with the best-fit fifth degree polynomial.

a distance between  $\delta$  and  $\delta+d\delta$  from the nearest point on the interface [1].

We employ the following algorithm to determine the pore-size function  $P(\delta)$  [33]:

- (1) Choose a random location in the pore phase.
- (2) Find the radius of the largest sphere centered at the above point that just touches the two-phase interface.
- (3) Repeat steps (1) and (2) for many random locations and create a list of radii.
- (4) After sampling sufficiently, bin the sphere radii. Divide the number of radii in each bin by the total number of radii to determine  $P(\delta)$ .

The interpolated functional form of  $P(\delta)$  is given in Eqs. (7)–(10) for the Schwartz  $P$ , Schwartz  $D$ , Schoen  $G$  minimal surfaces, and the circular-channel model (spherical pore-circular channel model with  $b=0$ ), respectively (see Fig. 4),

$$P(\delta) = \begin{cases} -149\delta^5 + 166\delta^4 - 61.2\delta^3 + 8.2\delta^2 - 0.696\delta + 0.164 & \text{if } \delta < 0.419 \\ 0 & \text{otherwise,} \end{cases} \quad (7)$$

$$P(\delta) = \begin{cases} 2238\delta^5 - 523\delta^4 - 44.1\delta^3 + 12.8\delta^2 - 1.55\delta + 0.275 & \text{if } \delta < 0.202 \\ 0 & \text{otherwise,} \end{cases} \quad (8)$$

$$P(\delta) = \begin{cases} -1388\delta^5 + 897\delta^4 - 225\delta^3 + 23.4\delta^2 - 1.47\delta + 0.223 & \text{if } \delta < 0.234 \\ 0 & \text{otherwise,} \end{cases} \quad (9)$$

$$P(\delta) = \begin{cases} -162\delta^5 + 173\delta^4 - 59.9\delta^3 + 7.57\delta^2 - 0.764\delta + 0.176 & \text{if } \delta < 0.234 \\ 0 & \text{otherwise.} \end{cases} \quad (10)$$

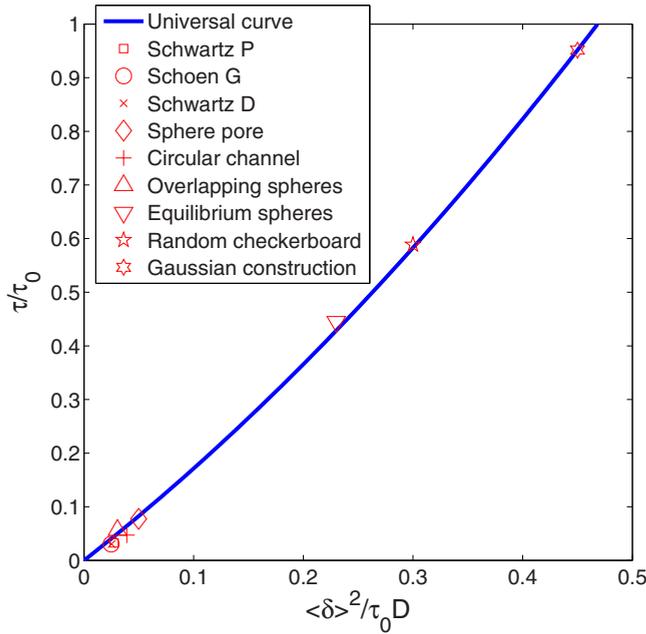


FIG. 5. (Color online) The dimensionless mean survival time,  $\tau/\tau_0$ , versus the scaled mean pore size squared,  $\langle \delta \rangle^2/(\tau_0 D)$ , for various two-phase media. The solid curve is the universal scaling relation (12) [28].

For the spherical pore (spherical pore-circular channel model with  $a=0$ ), the pore-size density function is exactly known,

$$P(\delta) = \begin{cases} \frac{3(a-\delta)^2}{a^3} & \text{if } \delta < a \\ 0 & \text{otherwise.} \end{cases} \quad (11)$$

**B. Universal curve**

Based on rigorous lower bounds on the survival time [1], the following universal scaling relation for  $\tau$  has been found to apply to a wide class of microstructures and range of porosities [28]:

$$\frac{\tau}{\tau_0} = \frac{8}{5}x + \frac{8}{7}x^2, \quad (12)$$

where  $\tau_0 = 3\phi_2/(D\phi s^2)$ ,  $x = \langle \delta \rangle^2/(\tau_0 D)$ , and  $\langle \delta \rangle$  is the mean pore size, defined by the first moment of the pore-size density function  $P(\delta)$  [1],

$$\langle \delta \rangle = \int_0^\infty \delta P(\delta) d\delta. \quad (13)$$

To explore the robustness of the universal curve, we check if the reported mean survival time data for a subset of the triply periodic surfaces fall on the curve. In order to compare the reported  $\tau$  results to Eq. (12), we determine  $\langle \delta \rangle$  from the pore-size density function  $P(\delta)$  results given above. Figure 5 reveals that the scaled survival times of the minimal surfaces fall relatively close to the universal curve. The cor-

responding values for the other bicontinuous structures considered here are close to the minimal-surface values and hence are not shown in the figure.

**VI. CONCLUSIONS AND DISCUSSION**

To conclude, we have shown that a simply connected pore phase is a crucial topological feature required to achieve large mean survival times at a porosity  $\phi=1/2$ . However, a simply connected pore phase is not a sufficient feature; one must also have interfaces with small specific surface  $s$ . Indeed, we found that the survival times are inversely proportional to the corresponding specific surfaces for all of the triply periodic structures considered here. Nonetheless, the pore spaces of structures with large survival times are expected to be simply connected and therefore it would not be unreasonable for  $\tau$  to be inversely proportional to the specific surface in these instances. We have demonstrated, as hypothesized, that the Schwartz  $P$  porous medium maximizes the mean survival time among the set of twelve triply periodic structures considered here. This lends further evidence to the multifunctional optimality of the Schwartz  $P$  minimal surface, making this structure of great practical value to guide the design of new materials with a host of desirable bulk properties. Moreover, scaled survival times of the minimal surfaces fall relatively close to the universal curve (12) found in Ref. [28].

Based on our findings, we conjecture that the mean survival time (like the fluid permeability) is maximized for triply periodic porous media with a simply connected pore space at porosity  $\phi=1/2$  by the structure that globally optimizes the specific surface. The verification of this conjecture remains an outstanding open question. This extremal problem falls in the general class of *isoperimetric problems*, which are notoriously difficult to solve. A prototypical isoperimetric example is Kelvin’s problem: the determination of the space-filling arrangement of closed cells of equal volume that minimizes the surface area. Although it is believed that the Weaire-Phelan structure [34] is an excellent solution to Kelvin’s problem, there is no proof that it is a globally optimal one. Our conjecture is also likely a difficult one to prove.

In this regard, it is noteworthy that an original goal of Ref. [15] was to show that the triply periodic surface with minimal specific surface  $s$  at porosity  $\phi=1/2$  is the Schwartz  $P$  surface. While numerical simulations provided empirical evidence supporting this proposition, the authors of Ref. [15] could not prove it rigorously. However, they were able to show that the Schwartz  $P$ , Schwartz  $D$ , and Schoen  $G$  minimal surfaces are local minima of the specific surface area  $s$  at fixed volume fraction  $\phi=1/2$ . Thus, the question of the global optimality of the Schwartz  $P$  surface (i.e., minimal total interface surface area or specific surface  $s$ ) is an open question for future investigation.

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