Rational Fabrication of High-Performance and Scalable Opal Crystals for Thermo-Fluidic Applications

by

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Abstract

Inverse opals have continuously attracted interest as a scalable, ordered porous material capable of enhancing energy, fluid, mass, or ion transport in a wide variety of applications. In particular, in heat transfer applications they have been used as porous coatings for condensers and boilers for increased efficiency in steam power plants and in two-phase thermal management devices with the potential of enabling next-generation electronic devices with high power density. However, several challenges remain with the fabrication of high-performance inverse opals due to limitations and defects of the initial opal template that ultimately prevent these structures from fulfilling their potential.

In this thesis, we first present a review of opal fabrication techniques and their implementation in heat transfer applications. We highlight previous challenges using these methods to achieve highly permeable structures in a simple way and we introduce slope self-assembly as a means to overcome several of these challenges. Despite its potential, we describe how fundamental understanding of this method is lacking, which limits its use with an arbitrary sphere size.

Second, in order to address this limited understanding, we develop a scaling-based model to elucidate the self-assembly process. Our model predicts the existence of two regimes: a gravity-driven flow regime for small colloidal particles, where the process is dominated by fluid flow, and a capillary-driven regime for large colloidal particles where the capillary forces between spheres dominate the process. With this model, we are able to predict and control the opal coverage on the substrate as a function of the experimental parameters.
Third, we perform experimental validation of our model by fabricating opal samples under different combinations of sphere sizes, colloidal concentrations, slope angles, and temperatures and analyze these samples with a custom image processing code. Our results confirm the validity of our model: for spheres smaller than 2 μm, the process is dominated by gravity-driven flow and the coverage can be controlled by changing the temperature, angle of inclination of the substrate, colloidal concentration, and sphere diameter, while for spheres larger than 10 μm the process is dominated by the capillary-driven flow and it can be controlled by changing the initial volume of solution, the concentration, and the sphere size.

Finally, we use the insights generated by our model to rationally fabricate millimeter-scale samples with monolayer coverage with sphere sizes between 500 nm to 10 μm, which is 10 times larger than the sphere size possible with the vertical deposition method, which has been commonly used for thermo-fluidic applications. Even larger, centimeter-scale samples are possible with some sphere stacking or small uncovered areas. Additionally, we show how this method can be used in a copper substrate, showing its applicability in heat transfer applications. Lastly, we highlight some future opportunities based on our work including the fabrication of multi-porous structures and the experimental tuning of the crystallinity of the opals while maintaining large-scale area coverage.

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Chapter 1

1. Introduction

1.1 Motivation

Porous materials have been proposed and implemented in a wide range of heat and fluid transport applications to enhance energy conversion and transport efficiency. Such advances have enabled significant improvements in current technologies as well as the development of new ones. For instance, the continual pursuit towards electronic component miniaturization over the last decades has been possible due to efficient heat and fluid transport in microporous wicks which have dissipated chip power densities approaching 100 W/cm\(^2\)\(^1\). Moreover, emerging technologies used in phased array radars, laser diodes, and high-power RF amplifiers demand even further improvements in these cooling technologies in order to meet power densities of approximately 5000 W/cm\(^2\)\(^2\).

Porous materials have also been proposed as a way to enhance heat transfer in condensers and boilers. These components are currently widely used in combined-cycle, coal, nuclear, and geothermal power plants which amount to more than 75% of all electricity generated in the United States\(^3\). Several previous studies have pointed to the potential of implementing porous coatings in power generation boilers and condensers as a way to enhance heat and fluid transport which can lead to higher heat-to-electricity conversion efficiency, reduced costs of electricity, higher safety operating margins, and less water consumption\(^4,5\). However, previous approaches have been limited by their lack of scalability, which has hindered their practical use in power plants.

Thus, as the performance of these porous materials dictates the device performance in all the applications previously mentioned as well as many others, it becomes critical to fabricate porous materials that can optimize transport in them while also being scalable so that they can be deployed at the desired scale. In addition, due to the varied requirements of the applications where porous materials are used, an ideal fabrication approach would be tunable to allow different characteristic pore sizes, porosities, and solid frameworks; in this way the relevant properties can be chosen such that the performance in a given application is optimized. Such a scalable, tunable, and high-performance approach can therefore lead to significant progress in many applications by reducing greenhouse gas emissions in power generation and enabling next-generation electronics.
1.2 Background

Porous materials possess many relevant properties that have made them ubiquitous in nature and in technological applications. By being composed of a solid matrix and void spaces, they can be engineered to transport heat, fluid, mass, ions, and electrons in the desired manner according to the specific application of interest. In particular, many heat transfer applications have utilized porous materials as a way to promote efficient heat transfer in the solid framework while simultaneously facilitating fluid or mass transfer through the void spaces.

Due to the fundamental differences in the applications where porous media are used, the requirements of the optimum media will be significantly different to be able to optimize the desired transport. Therefore, a detailed understanding of the relevant phenomena in each application is needed to be able to design the media, provided that the fabrication method for the porous material provides the flexibility to achieve the optimum features.

Figure 1. Examples of heat transfer applications that can use porous materials to enhance their performance include a) capillary-fed thermal management, b) wicking condensation, and c) pool boiling with a porous coating. These applications rely on simultaneous fluid transport in the empty parts of the porous material, while thermal energy is transferred in the solid parts.

1.1.1 Thermal management

Porous wicks form a critical component in heat pipes, which have been widely used as a thermal management solution to regulate the temperature of electronic components. In a heat pipe, a porous wick
will serve as a porous evaporator to dissipate heat generated in the electronics (Figure 1a). The porous wick fulfills three different functions in these systems: 1) It provides a thermally conductive path for heat to be conducted easily from the source to the evaporating interface, 2) it provides a path for liquid resupply to balance the vapor that is leaving the system, 3) it provides a capillary driving force for resupplying liquid passively\(^6\). In order to fulfill these requirements, wicks have been traditionally manufactured with porous metals with characteristic pore sizes of \(\sim 100 \, \mu m\)\(^7\). The thickness of these wicks is chosen such that they have a pressure drop smaller than the capillary pressure generated in its pores while simultaneously being thin to reduce its thermal resistance\(^8\).

However, novel electronic technologies with significant promise like gallium nitride high electron mobility transistors (GaN HEMTs) pose even greater thermal management challenges as they generate heat fluxes higher than the heat that can be removed in traditional heat pipes\(^9\). Additionally, without improved thermal management technologies, the high heat fluxes in HEMTs will lead to higher electronic temperatures, which can exponentially shorten the lifetime of these components\(^10\). In order to address these higher temperatures and higher heat fluxes, many new approaches have been explored as a way to enhance the heat transfer performance (as quantified by the heat transfer coefficient, HTC) and to be able to withstand the high energy densities (as quantified by the critical heat flux) as shown in Figure 2.
These experiments have demonstrated the ability to overcome previous limitations by fabricating highly ordered porous media that facilitate fluid resupply, which in turn allows having thinner wicks with higher heat transfer coefficients. However, these approaches have relied on complex and expensive microfabrication processes, on active pumping for liquid resupply which can also cause flow instabilities, or on very small cooling areas (< 1 mm²). There is, therefore, a need for a scalable, large-area (>1 mm²), passive approach that can efficiently handle the power densities of emerging technologies (> 1 kW/cm²).
1.1.2 Condensation

Condensation heat transfer can also be enhanced by implementing porous materials in applications like steam power generation with the goal of reducing the need for cooling water in an industry that is the highest consumer of water in the United States\textsuperscript{20} and lowering the condenser temperature and pressure, which can lead to increased power outputs\textsuperscript{21}. Previous research on condensation enhancement has focused on promoting dropwise condensation\textsuperscript{22} and jumping droplet condensation\textsuperscript{23} by using superhydrophobic coatings and nanostructures. However, these approaches have shown significant durability issues within hours or weeks\textsuperscript{24} due to the coatings required to harness these behaviors.

Porous materials offer a durable alternative to achieve similar enhancements in heat transfer. By promoting condensation in a thermally conductive porous wick, the effective thermal conductivity of the condensed liquid film can be reduced compared to the film being pure liquid (Figure 1b). Research in this condensation mechanism has shown that the porous medium will be susceptible to heat transfer degradation if the wick has low permeability and if gravity is not able to drive condensate outside of the porous material fast enough\textsuperscript{25}. This can be overcome by having a pump to assist the removal of condensate\textsuperscript{26} at the expense of additional system complexity and cost, as well as additional energy consumption. These challenges can be mitigated by implementing highly porous and highly permeable porous materials that will be less susceptible to flooding while also providing significant heat transfer enhancement by using a metallic solid matrix.

1.1.3 Pool boiling

In addition to steam condensation, steam generation, which is widely used in space heating, desalination, and power generation, can also be improved by using a porous medium (Figure 1c). Specifically, previous research has shown that the critical heat flux (CHF) and the heat transfer coefficient (HTC) in pool boiling can be enhanced by using microstructures that promote quick liquid rewetting and fast bubble dynamics\textsuperscript{27}.

Porous materials can provide a scalable alternative to complex microfabricated structures to provide significant CHF and HTC enhancements\textsuperscript{28,29}. Previous work has shown that the enhancements achievable are limited by competing viscous and capillary effects\textsuperscript{30,31}, and therefore, further performance improvements can be achieved by improving the permeability of these porous materials.
1.1.4 Other applications

In addition to the applications mentioned before, porous media are used in multiple other heat and fluid transport applications due to their many useful and tunable properties. They have been used as thermally conductive supports for sorbents in atmospheric water harvesting\(^ {32}\) and in thermal energy storage applications\(^ {33}\). In these applications, these media need to be optimized to transport heat efficiently while being highly porous to facilitate vapor transport and maximize sorbent content. Passive, sun-powered desalination can also be enabled by porous materials which provide capillary wicking and permeable pathways for fluid resupply to the evaporating interface\(^ {34,35}\).

Many other fields other than heat transfer benefit from using porous materials as a way to optimize transport. Numerous chemical and electrochemical applications rely on porous materials to provide enhanced surface area for chemical reactions to occur including electrodes in lithium-ion batteries\(^ {36}\) and gas evolution electrodes, where, analogously to pool boiling, the porous material can influence bubble dynamics and impact the overall device performance\(^ {37}\).

1.3 Thesis objectives and outline

The objectives of this thesis are: 1) to obtain a better understanding of the fabrication of opal crystals, which can be used as a template for high-performance porous materials, with the slope self-assembly method and 2) to use the knowledge generated to fabricate opal structures in a rational way with arbitrary pore sizes for applications introduced above. Details about the content of this thesis are outlined below:

In Chapter 1 we discuss the motivation for the fabrication of porous materials in different applications, with a particular focus on heat and fluid transport applications. We highlight how, in spite of the differences between the applications mentioned, they all benefit from high permeability and good heat transport in the medium. In addition, we discuss how an ideal fabrication method that is able to work for all those applications would be able to produce porous structures with tunable properties.

In Chapter 2, we introduce inverse opals as a promising, high-performance porous material for thermo-fluidic applications. In particular, we review slope self-assembly as a method to fabricate the ordered template for inverse opals and highlight the need for a fundamental understanding of this process to allow for fast and optimized fabrication.
In Chapter 3, we develop a scaling-based model for the slope self-assembly process to elucidate the relevant parameters of the process and the different regimes attainable. This model provides practical guidelines on how to control the coverage of opals on a structure by changing the different experimental parameters.

In Chapter 4, we perform experimental validation of the self-assembly model and show the good agreement between our model and experimentally obtained structures.

In Chapter 5, we leverage the insights provided by our model to fabricate large-scale monolayer structures with the slope self-assembly method with particle sizes ranging from 500 nm to 10 μm.

In Chapter 6, we provide conclusions and highlight some opportunities based on the knowledge obtained from our work. We discuss the potential for the fabrication of multi-porous materials with the slope-self-assembly method as well as the experimental optimization of the opal crystallinity, while also maintaining large-scale coverage.
Chapter 2

2. Inverse Opals

In this chapter, we introduce inverse opals as a microporous structure based on self-assembly templating with great promise for the thermo-fluidic applications described above. We review the most common fabrication methods for the opal template and the methods to modulate the inverse opal properties. Finally, we review past uses of inverse opals in heat transfer applications and introduce slope self-assembly as a method capable of addressing limitations in previous demonstrations.

2.1 Overview

Inverse opals consist of three-dimensional ordered microporous structures formed by infiltrating a solid material on a template made of a crystalline arrangement of spheres, called opal, and then removing the spheres. Due to the closed packed nature of the sphere template (see Figure 3), the resulting inverse opals will be highly porous, with porosities exceeding 75%. Additionally, since the template is highly regular, inverse opals will be a very ordered, low tortuosity medium, which in combination with the high porosities make them an ideal medium for fluid transport, as they will be characterized with flow permeabilities exceeding those of a random porous medium.

Figure 3. Schematic of opal crystal consisting in closely packed, monodisperse spheres arranged on a substrate.
Inverse opals have also attracted significant interest in many other applications. For instance, their high periodicity and characteristic pore sizes in the order of 100 nm – 1000 nm have made them attractive candidates for photonic crystals that can be used in optoelectronic circuits or as selective absorbers and emitters. Also, due to their optical properties, they can be used as colorimetric sensors of ion concentration and of relative humidity. Additionally, inverse opals exhibit high specific surface area, which can be used to promote chemical reactions effectively in catalytic applications and porous battery electrodes.

2.2 Colloidal self-assembly methods

The many applications in which inverse opals can be used impose different requirements of the original template’s order, porosity, and diameter of the spheres. For example, previous work has shown that optical and fluidic applications require opal crystals with a low density of crack defects as this can significantly reduce the structure performance. Also, particle diameter requirements can vary considerably between applications: smaller pore sizes will be better for applications where high surface area is desired, whereas large pore sizes will optimize fluid transport due to a lower viscous resistance. In order to meet the different requirements of inverse opals applications, many self-assembly methods have been developed to fabricate the opal template, which will usually be made of silica or polymer spheres, exhibiting varying degrees of order, complexity, throughput, as well as range of spheres that can be used. Some of the most common methods are:

- Sedimentation, in which the colloidal spheres self-assemble into polycrystalline structures after having been precipitated under the action of gravity. Despite its simplicity, this method suffers from extremely low throughput, where the self-assembly of a sample can take up to months, due to the low precipitation velocities for nanometer-sized particles. Additionally, templates generated with this technique will have numerous crystal defects, further limiting the applicability of this method.

- Centrifuged sedimentation, which relies on centrifugal forces for the accelerated precipitation of the colloidal particles. By using centrifugal forces which are stronger than gravitational forces on colloidal particles, the process can be faster than with regular sedimentation at the expense of the structure performance.
• Langmuir-Blodgett method, in which the colloidal solution is deposited in the liquid-vapor interface of a Langmuir trough and compressed to achieve close-packing. This close-packed monolayer can then be transferred into a substrate that is removed from the trough\(^52\). This method has shown high-quality crystals over relatively large areas (\(> 1 \text{ cm}^2\))\(^52\). However, it is also experimentally complex, susceptible to vibration during the substrate removal, and time-consuming due to its layer-by-layer nature\(^50,53,54\).

• Drop-casting, in which the colloidal solution is drop-casted on a flat hydrophilic surface. Evaporation of the solvents will cause thinning of the film covering the substrate until eventually, the thickness will be smaller than the particle diameter and particles will start self-assembling due to capillary attractive forces\(^55\). Despite its simplicity, this method yields structures with limited order and can suffer from highly non-uniform coverage due to the coffee stain effect which generates multilayers in the edges of the pinned drop and areas without opals in the center of the substrate\(^50,56\).

• Spin coating, similarly to drop-casting, relies on drop casting a solution in a flat substrate, with the difference that the solution will be spin-coated on the substrate, ensuring substrate coverage and providing more control of the process\(^57\). This process, however, can only yield highly ordered structures over small areas and on smooth substrates\(^58,59\).

• Vertical deposition, which consists in the evaporation of the colloidal solution with a hydrophilic substrate vertically submerged in the solution. In this method, as the solution evaporates, the meniscus of the solution attracts spheres to the substrate which will self-assemble on the surface. This method is able to generate highly crystalline structures with precise control of the number of layers\(^60\). However, opals formed with this method have been shown to always exhibit crack formation due to capillary forces generated during the drying process\(^61\). Additionally, this method is limited to small spheres (1 µm or less) since larger spheres will precipitate over the time span of the process\(^62\).

After the opal template has been deposited on the substrate, a solid material is infiltrated in between the spheres. This can be achieved by different techniques including electrodeposition\(^45,47\), chemical vapor deposition\(^63\), atomic layer deposition\(^64\), and sol-gel infilling\(^65\), providing different alternatives to deposit the material that is desired for a specific application. Once the solid material has been deposited, the spheres
can be removed by chemical or thermal etching, revealing an inverse opal with pores corresponding to the space left behind by the spheres.

2.3 Modulation of inverse opal properties

Inverse opal properties such as pore size, porosity, and thickness can be easily controlled as part of its fabrication process, which provides a way to optimize these properties for the desired application. Pore size can be controlled by the selection of the diameter of the colloidal spheres that are used to make the template. The inverse opal porosity can be controlled either by sintering the template\textsuperscript{51}, which causes sphere coalescence previous to infiltration and sphere removal or by electropolishing of the inverse opals\textsuperscript{66}, if they are made of an electrically conductive material. The thickness of the inverse opals can be controlled through the number of layers of spheres stacked on the substrate. This number of layers depends on the method used and, for example, can be controlled by changing the colloidal concentration in the vertical deposition method\textsuperscript{47} or by repeating the self-assembly process several times in layer-by-layer processes such as the Langmuir-Blodgett.

However, these parameters cannot be chosen in a completely arbitrary way in all self-assembly methods. Previous research has shown that above a certain critical thickness of the opal template, cracking and delamination from the substrate will occur\textsuperscript{51,67}. Similarly, not all particle diameters can be used with any method. For instance, vertical deposition will be limited to spheres below 1 µm due to undesired sphere sedimentation or conversely, the sedimentation method occurs quicker for larger spheres and it would be practically inviable for small spheres due to their small masses.

2.4 Inverse opals in heat transfer applications

Their high porosity, order, high thermal conductivity, and simplicity of fabrication have made inverse opals attractive in many different thermo-fluidic applications. However, in spite of their potential, previous demonstrations have had limited success, mostly due to limitations of the methods used to fabricate the initial opal template. As shown in Figure 4, opals that have been demonstrated in literature are limited in their permeability due to the disorder of the template, which causes deviations in their flow properties compared to an ideal structure\textsuperscript{68} or due to the small pores which present high viscous resistances (which are proportional to $1/D^2$, where $D$ is the pore diameter)\textsuperscript{7,47}.
Figure 4. Inverse opals properties in thermo-fluidic applications characterized by their pore size and order. Data reproduced from references 68-72. Sedimented opals were considered semi-ordered due to numerous defects they contain 49, while vertical deposition opals were considered ordered in spite of their crack defects due to their high permeability in the crystalline domains 47.

2.4.1 Capillary-fed boiling

Inverse opals have been used as high-performance, microporous media for extreme thermal management devices. In these systems, heat is dissipated with high heat transfer coefficients (HTCs) through boiling in the inverse opals, which also generate capillary pressures to compensate the liquid that is being lost by boiling. Palko et al. demonstrated exceptional cooling performance with inverse opals capable of dissipating heat fluxes above 1 kW/cm² with superheats below 10°C 17. However, this was only possible over a very small cooling area of less than 1 mm². Particularly, since the maximum heat flux that can be dissipated in a capillary-fed device scales as $I/L^2$ with $L$ being the length along which wicking is happening 6, the implementation of a similar approach on larger devices would require more permeable structures that can facilitate the liquid resupply across all the device.
The limitations of inverse opal structures can be partially addressed by sintering the initial opal template, which causes sphere coalescence and higher permeabilities\textsuperscript{69}, or by actively pumping the liquid, instead of relying solely on capillary pressure\textsuperscript{18}. Even further improvements are possible if larger pore sizes are used as well as more ordered templates. These strategies can be combined with a nanoporous membrane on top of the inverse opal wick to decouple viscous and capillary effects\textsuperscript{16}. Such a strategy can allow dissipating passively high heat fluxes over larger areas.

2.4.2 Pool boiling

Due to their regular and controllable morphology compared to random porous media, inverse opals are promising candidates to study the physics of pool boiling on sources that have porous coatings. Pham et al. studied pool boiling in nickel inverse opals of different pore sizes and different thicknesses. They observed that for a given pore size, there will be a thickness that optimizes the critical heat flux attainable, which originates from the competition between evaporation and vapor transport and that an intermediate pore size will maximize the heat transfer coefficient\textsuperscript{70}.

However, the mechanisms that lead to this result are still unclear. In particular, there is limited understanding of how the inverse opal morphology connects to critical boiling parameters like nucleation site density, bubble departure diameter, and bubble departure frequency. More in-depth knowledge of this connection between structure morphology and thermophysical phenomena can help design high-performance inverse opals for pool boiling to significantly improve the critical heat flux and heat transfer coefficient of pool boiling and can elucidate more of the complex, multi-physical phenomena that occur during boiling.

2.4.3 Condensation

Inverse opals have also attracted interest as porous coatings to enhance the heat transfer coefficient of condensers. Oh et al. fabricated nanoporous inverse opals with a thin (<20 nm) hydrophobic coating as an alternative to non-durable hydrophobic coatings on flat surfaces. By applying the hydrophobic coating, the liquid film can be constrained to a thin film with a high effective thermal conductivity, due to the thermally conductive nature of the inverse opals. In addition, since condensation does not occur on the hydrophobic coating, but it occurs instead inside the inverse opal, durability issues can be mitigated\textsuperscript{71}.

In their work, they showed that large pore sizes are necessary to achieve high heat transfer enhancements due to their smaller viscous resistances\textsuperscript{71}. However, in practice, opal defects will limit the achievable
enhancement due to the reduction of permeability. On the other hand, these defects can be leveraged to improve the thermo-fluidic performance of the condenser. For instance, Adera et al. showed that the preferential liquid transport along opal cracks can be leveraged to facilitate liquid transport in an inverse opal condenser, showing a more than six-fold enhancement in the heat transfer coefficient compared to filmwise condensation on a smooth surface\textsuperscript{72}.

2.5 Slope self-assembly

The limitations in previous opal fabrication methods motivated us to explore new fabrication alternatives with superior permeability, which can be achieved by reducing defects and increasing pore size, while still being scalable, simple, and have high throughput. In this work, we study slope self-assembly\textsuperscript{59,73–75}, also referred to as inclined drop-casting, as a simple fabrication method with the potential to address the limitations mentioned before.

In slope self-assembly, the colloidal solution is drop-casted on an inclined hydrophilic substrate. The solution quickly spreads the substrate, driven by capillarity and gravity, until it fully covers the substrate. Then, gravity and evaporation will cause the film thickness ($h(x, t)$) to continuously decrease, where the thinnest region is on the upper part of the substrate, where sphere self-assembly starts (Figure 5).

![Figure 5. Schematic of the slope self-assembly process. The fluid thickness decreases driven by gravity and by evaporation. The fluid influences sphere self-assembly via drag forces $F_{drag}$. $\theta$ is the angle of inclination of the substrate, $\dot{m}''_{evap}$ is the evaporation rate flux, and $h(x, t)$ is the thickness of the fluid film containing the colloidal particles. Figure 6 shows a time-lapse images of the slope self-assembly method on a glass](image)
substrate. Initially, the solution covers the entire substrate (Figure 6a). Then, as the upper part parts of the substrate are dried, some spheres are left behind on the substrate while others are dragged with the fluid. As the liquid contact line moves down along the substrate, a coating of spheres is formed (Figure 6b). This coating can fully or partially cover the whole substrate, depending on the solvents, temperatures, concentrations, and angles used in the process\textsuperscript{59}. When all the solvents have evaporated, only spheres are left in the substrate forming a partial or total coating (Figure 6c).

**Figure 6.** Time-lapse images of the slope self-assembly process on a 75° slope with a colloidal solution with 1 µm spheres. a) The solution is drop-casted on the inclined substrate and it spreads to cover all the substrate. b) As evaporation and liquid motion cause the contact line to move across the substrate, spheres are left behind in the dry area. c) When all the solvent has evaporated, a coating of spheres is left on the substrate. Improper selection of the angle, temperature, and colloidal concentration can yield significant empty parts. Scale bars are 1 mm.

Previous work using this opal fabrication approach has shown that in spite of being as simple as drop-casting, this method can generate structures with more order and controlled coverage than drop-casted opals, partially since there are more parameters that can be experimentally controlled to optimize the resultant structures, including the angle of inclination. Additionally, since the contact line moves across the substrate (Figure 6) and it is not pinned, as would be the case in drop-casting on a flat surface, there will be less coffee-stain effect. This effect will only occur near the edges of the substrate, where droplet pinning is still present\textsuperscript{56}. Moreover, due to the short time needed to fabricate the opals, which also translates into high-throughput, the spheres are less prone to precipitating, which has allowed previous researchers to fabricate opals with this method with particle sizes as small as 46 nm and up to 1.7 µm\textsuperscript{73,74}. 

25
Previous studies on this method have experimentally shown the relevance of the angle of inclination, solvents, temperature, and concentration in achieving coverage of large areas of the substrate and in the order of the opals\(^{59,75}\). These studies have been able to empirically optimize those parameters for a specific particle size through trial and error. There is, however, a lack of fundamental understanding of the process which impedes the application of this method to self-assembly of arbitrarily-sized particles in a simple and fast manner. Such fundamental understanding can enable the fast and rational fabrication of high-quality opals, and therefore inverse opals, with larger pore sizes than what has been shown previously in thermo-fluidic applications.

2.6 Summary

In summary, this chapter introduced inverse opals as promising porous materials for thermo-fluidic applications. Numerous fabrication methods of the opal template have been developed with varying degrees of complexity and structure quality. However, current demonstrations of inverse opals in thermo-fluidic applications have shown limited performance due to their small pore sizes and prevalence of defects in the opal templates. To overcome these challenges, we proposed to use the slope self-assembly method as an alternative for the opal template fabrication. We reviewed research on this method and showed that in spite of the success of this method in achieving simple, ordered structures, there is limited fundamental understanding of the process which can guide the rational and facile fabrication of these structures for a wide range of applications.
Chapter 3

3. Slope Self-Assembly Model

Previous theoretical analyses of the slope self-assembly method have either been in terms of variables that are difficult to control experimentally, such as the array growth rate\textsuperscript{74}, or have only analyzed the dominant interactions between colloidal particles, without providing practical guidelines for the fabrication of these structures\textsuperscript{59}.

Here, we formulate a scaling-based model for the self-assembly process in order to elucidate the role of the different fabrication parameters (colloidal concentration, inclination angle, temperature, sphere diameter, solvents used) in the resulting structures. In particular, we seek to predict the fraction of the substrate that will be covered with the opal as this is a critical parameter in order to ensure connectivity of the inverse opal in thermo-fluidic transport as well as in other applications including biomolecule printing, whereby maximizing the coverage of opals, the quality, and throughput of single-molecule images can be optimized\textsuperscript{76}.

3.1 Formulation of self-assembly model

We initially consider the regime where the fluid dynamics of the solvent dictates completely the motion of the colloidal particles and therefore, we focus on describing the fluid film evolution to predict the dynamics of the opals.

We first define the coverage fraction as the fraction of the substrate area covered by spheres which is the parameter that we want to predict with our model

\[
\text{Coverage fraction} = \frac{N_{\text{spheres}} A_{\text{sphere}}}{A_{\text{sub}}},
\]

where \( N_{\text{spheres}} \) is the number of spheres left in the region of interest of the substrate with area \( A_{\text{sub}} \) and \( A_{\text{sphere}} = \pi D^2 / 4 \) is the projected area of a sphere. The number of spheres left on the substrate is determined by how much solvent flows out of the area of interest

\[
N_{\text{spheres}} = \frac{(V_0 - Q \tau) C}{V_{\text{sphere}}}.
\]
where $V_0$ is the volume of solution drop-casted, $\dot{Q}$ is the average net volumetric flux of solvent leaving the region of interest due to gravity-driven flow (See Figure 7), $\tau$ is the timescale of the self-assembly process, $C$ is the colloidal concentration and $V_{\text{sphere}} = \pi D^3 / 6$ is the volume of a colloidal particle. $\dot{Q}$ is obtained by considering solvent conservation, where the initial known amount of solvent will either be evaporated or flow due to gravity

$$V_0 (1 - C) = \dot{Q} \tau (1 - C) + \frac{\dot{m}''_{\text{evap}} A_{\text{sub}} \tau}{\rho},$$

where $\rho$ and $\dot{m}''_{\text{evap}}$ are the density and evaporation flux (kg/m$^2$ s) of the solution, respectively.

Figure 7. Schematic of the model for self-assembly process. Substrate coverage and film thickness are governed by gravity and evaporation.

Equations 1, 2, and 3 can be combined to obtain

$$\text{Coverage fraction} = \frac{3\dot{m}''_{\text{evap}} \tau C}{4 \rho D (1 - C)}$$

which gives the desired coverage fraction in terms of parameters that can be controlled experimentally and the timescale of the process.

This timescale is given by the dynamics of the film. We use the lubrication approximation to extract this timescale from the fluid mechanics physics of the process. To do this, we scale the different forces with the following parameters:
(i) Film thickness scale: 
\[ h \sim h_0 = \frac{V_0}{A_{\text{sub}}} \sim 10 \frac{\mu L}{4 \text{cm}^2} = 2.5 \cdot 10^{-5} \text{ m} \]

(ii) Length scale in the flow direction: 
\[ x \sim L \sim 2 \cdot 10^{-2} \text{ m} \]

(iii) Timescale: 
\[ \tau \sim 400 \text{ s} \]

(iv) Velocity scale: 
\[ U \sim \frac{L}{\tau} = 5 \cdot 10^{-5} \frac{\text{m}}{\text{s}} \]

Angle of inclination: \[ \theta \sim 30^\circ \]

where \( h_0 \) is the initial film thickness and \( L \) is the length of the substrate in the flow direction. These parameters are based on our experimental conditions and observations. For the thermophysical properties, we use the order of magnitude of ethanol-water mixtures at room temperature:\(^7\)

- Density: \( \rho \sim 1000 \frac{\text{kg}}{\text{m}^3} \)
- Viscosity: \( \mu \sim 1 \cdot 10^{-3} \text{ Pa} \cdot \text{s} \)
- Surface tension: \( \sigma \sim 0.1 \text{ N/m} \)

With the previously defined scales, we can determine the dominant forces acting on the fluid film and simplify the governing equations. We start from the Navier-Stokes equations in the \( x \) and \( y \) direction (Figure 7) and mass conservation for the velocity field \( \vec{v} = (v_x(x,y), v_y(x,y)) \) and the pressure field \( P(x,y) \)

\[
\rho \left( \frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} + v_y \frac{\partial v_x}{\partial y} \right) = -\frac{\partial P}{\partial x} + \rho g \sin \theta + \mu \left( \frac{\partial^2 v_x}{\partial x^2} + \frac{\partial^2 v_x}{\partial y^2} \right),
\]

\[
\rho \left( \frac{\partial v_y}{\partial t} + v_x \frac{\partial v_y}{\partial x} + v_y \frac{\partial v_y}{\partial y} \right) = -\frac{\partial P}{\partial y} - \rho g \cos \theta + \mu \left( \frac{\partial^2 v_y}{\partial x^2} + \frac{\partial^2 v_y}{\partial y^2} \right),
\]

\[
\frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} = 0,
\]

We simplify these equations by considering locally fully developed flow to

\[
0 = -\frac{\partial P}{\partial x} + \rho g \sin \theta + \mu \left( \frac{\partial^2 v_x}{\partial y^2} \right),
\]

\[
0 = -\frac{\partial P}{\partial y} - \rho g \cos \theta,
\]

which hold since\(^7\)

(i) \[ \frac{\rho h_0}{\mu \tau} \sim 1 \cdot 10^{-6} \ll 1 \]

(ii) \[ \frac{h_0^2}{L^2} \sim 1 \cdot 10^{-6} \ll 1 \]

(iii) \[ (\rho U L/\mu)(h_0^2/L^2) \sim 1 \cdot 10^{-6} \ll 1. \]
Equation 9 can be integrated and substituted in Equation 8. In particular, the pressure term in Equation 8, which can have contributions due to gravity and due to surface tension, will be negligible compared with the gravity term since

\[(i) \quad \frac{h_0}{L} \cot \theta \sim 1 \cdot 10^{-3} \ll 1\]
\[(ii) \quad \frac{\sigma h_0}{l^2 \rho g \sin \theta} \sim 6 \cdot 10^{-5} \ll 1\]

With this, the pressure term can be neglected in Equation 8 and the velocity profile can be integrated

\[v_x = \frac{\rho g}{\mu} \sin \theta \left( h_y - \frac{y^2}{2} \right), \tag{10}\]

which can be combined with mass conservation for the film to result in the lubrication approximation equation for the film thickness evolution

\[\frac{\partial h}{\partial t} + \frac{\rho g h^2 \sin \theta}{\mu} \frac{\partial h}{\partial x} + \frac{m''_{\text{evap}}}{\rho} = 0, \tag{11}\]

From Equation 11 it can be seen that the gravity term will dominate when the film thickness is large and the thickness reduction will be dominated by gravity-flow effects. However, as the film decreases in thickness, evaporation will become comparable, which happens when the thickness reaches a characteristic value given by the balance of gravity and evaporation

\[h_{\text{char}} = \left( \frac{L \mu m''_{\text{evap}}}{\rho^2 g \sin \theta} \right)^{1/3}. \tag{12}\]

The thickness will continue decreasing past this characteristic value. Eventually, the thickness will reach a small value such that evaporation will be dominant. As a result, it is possible to distinguish two possible regimes for the process. If the initial thickness is smaller than \(h_{\text{char}}\), the gravity term in Equation 11 can be neglected and we can describe the process with the timescale given by pure evaporation

\[\tau_{\text{evap}} = \frac{\rho h_0}{m''_{\text{evap}}}. \tag{13}\]

For practical use of this opal fabrication method, this will be the case only at very low inclination angles, which imply large \(h_{\text{char}}\). In this limit, the process will be similar to drop-casting on a flat surface where only evaporation is occurring and no spheres are leaving the substrate.
Most commonly, for solutions with thermophysical properties similar to those of water-ethanol mixtures and for intermediate angles ($\theta = 20^\circ - 90^\circ$), $h_0 \gg h_{\text{char}}$ and gravity is significant. In this case, the timescale is given by the time it takes the film to go from $h_{\text{char}}$ to a fully dry sample, given by

$$\tau_{\text{grav}} = \left( \frac{\mu L \rho}{\dot{m}''_{\text{evap}} g \sin \theta} \right)^{1/3},$$

This timescale, which is the most relevant for practical use of slope self-assembly, can be combined with Equation 4 to obtain

$$\text{Coverage fraction} \sim \left( \frac{\mu L \dot{m}''_{\text{evap}}}{\rho^2 g \sin \theta} \right)^{1/3} \frac{C}{(1 - C)D},$$

which gives us the desired expression of the coverage fraction of opals on the substrate in terms of parameters that can be experimentally controlled like the solvents, evaporation rate $\dot{m}''_{\text{evap}}$ (which is determined by temperature, relative humidity and solvents used), colloidal concentration $C$, particle diameter $D$, and substrate inclination angle $\theta$.

### 3.2 Effect of capillary forces

In the previous discussion, it has been assumed that the motion of the spheres is completely determined by the fluid motion via drag forces exerted by the fluid on the particles. These forces can be estimated with the Stokes law

$$F_{\text{Drag}} = 3\pi \mu DU,$$

which is valid since the Reynolds number of the colloidal spheres is small

$$Re = \frac{\rho UD}{\mu} \approx 5 \cdot 10^{-5} \ll 1,$$

for particles of 1 $\mu$m diameter.

However, it is also well known that capillary forces play an important role in colloidal self-assembly by promoting close packing of spheres into a crystalline array$^{79}$ and even playing a fundamental role in the formation of defects$^{61}$. These capillary forces can have different possible physical origins. If the spheres are floating on the liquid-vapor interface (Figure 8a), they will deform the interface due to their weight.
originating the so-called flotation forces. These flotation forces will be attractive for particles with the same contact angle and they scale as 79

\[ F_{\text{Flotation}} \sim \frac{D^6}{\sigma} K_1(l/l_c), \]  

(18)

where \( K_1 \) is the modified Bessel function of the 1st order, \( l \) is the interparticle distance, and \( l_c = \left( \frac{\sigma}{\rho g} \right)^{0.5} \) is the capillary length of the solvents.

![Flotation forces](image)

![Immersion forces](image)

**Figure 8.** Types of interparticle capillary forces in colloidal self-assembly. Depending on whether the spheres are floating in the liquid-vapor interface or protruding out of a liquid film thinner than the sphere diameter, the forces can be either flotation forces or immersion forces.

On the other hand, if the spheres are larger than the liquid film thickness, they protrude out of the film and a meniscus is formed around the spheres (Figure 8b). The meniscus causes capillary attractive forces between similar colloidal particles, which are referred to as immersion forces. In the limit of large interparticle separation compared with the capillary length and for particles of the same diameter the immersion forces scale as 79

\[ F_{\text{Immersion}} \sim \sigma D^2 K_1 \left( \frac{l}{l_c} \right), \]  

(19)

It should be noted that these flotation and immersion forces scale as \( \sim D^6 \) and as \( \sim D^2 \), respectively, which means that they grow faster with particle diameter than the drag force given by Equation 16. This suggests the existence of a regime at large sphere sizes where these capillary forces not only promote the close-
packing of spheres, but also significantly cause a deviation of the spheres motion compared to that of the liquid film due to a comparably smaller drag.

We consider the limiting case of this regime, where we can neglect completely liquid drag and consider only capillary attractive forces between colloidal particles. In particular, as shown in Figure 9, spheres that are in the liquid-vapor interface attract each other due to the flotation forces. In the upper part of the substrate, where the film is thinnest, the spheres protrude out of the solvents and generate capillary attractive forces that close-pack them but that also attract other spheres from lower parts of the liquid film, pulling them against gravity to expand the opal crystal.

Figure 9. Schematic of the capillary-dominated regime of slope self-assembly, where liquid drag is negligible compared to capillary interactions. In this regime, spheres motion is dominated by interparticle attraction forces due to capillarity $F_{\text{cap}}$.

With negligible liquid drag occurring, no spheres are lost at the bottom of the substrate, and we can consider $\dot{Q} = 0$ in Equation 2. We can then combine Equations 3 and 4 to obtain an expression analogous to Equation 15, but for the capillary-dominated regime

$$\text{Coverage fraction}_{\text{capillary}} = \frac{V_0 C A_\text{sphere}}{A_{\text{sub}} V_\text{sphere}} = \frac{3V_0 C}{2DA_{\text{sub}}}. \quad (20)$$

This expression, analogously to Equation 15, allows us to predict and rationally control the coverage of opals on the substrate for large particles by controlling the volume of solution used and the colloidal concentration for a given sphere diameter and substrate area.
It should be noted that the transition between the capillary regime and the gravity-driven flow regime not only depends on the diameter dependence of the drag and capillary forces (Equations 16, 18, 19), but also on the relative sizes of the initial film thickness and the sphere diameter. For instance, if the spheres are comparable to the initial film thickness, they protrude earlier outside of the film, providing them with more time to attract other spheres via their capillary forces. On the other hand, smaller spheres only protrude when the film thickness is small, giving them less time to attract other spheres since the film evaporates quicker.

3.3 Summary

In this chapter we developed a scaling-based model for the slope self-assembly process that allows to predict the fraction of area of the substrate that is covered by opal as a function of experimentally controllable parameters which is valid for small spheres. This model can help experimentalists that for their given application require a particular sphere size to choose the temperature, concentration, solvents, and angle at which they should perform the process.

We also noted the presence of a different regime, in which the process is dominated by capillary interaction forces instead of liquid drag. We analogously derived an expression for the area coverage in this regime, which can be used to fabricate opals with large particle sizes.
Chapter 4

4. Experimental Validation

Having developed a model that allows to predict the fraction of substrate covered by spheres as a function of the different experimental parameters, we performed in-depth experimental validation of this model by fabricating different opal samples under different combinations of sphere diameter, angle of inclination, temperature of the solution, and colloidal concentration.

4.1 Experimental methods

Colloidal solutions were prepared from polystyrene microbead solutions with sphere sizes of 500 nm, 1 µm, 2 µm, 10 µm, 30 µm (Sigma). The microbeads were centrifuged out of the stock solution. The supernatant was removed and the beads were resuspended in DI water, centrifuged once more, and then resuspended in 25% volume of ethanol and 75% volume of DI water, to the desired concentration. The solution was vortexed vigorously to ensure uniformity and resuspension of the polystyrene.

Microscope cover glasses (Sigma, 1.8 cm x 1.8 cm) were used as substrates. The cover glasses were cleaned with oxygen plasma (10 min, 11 W) to make them hydrophilic, ensuring quick and uniform spreading of the solution on the substrate. The prepared colloidal solutions were vortexed again and a volume of approximately 10 µL was drop-casted on the glass slides. The solution was left to evaporate to the ambient. Throughout all the experiments, room temperature was between 23.6 °C and 25.3 °C and relative humidity was between 41.1% and 48.3%.

To study the gravity-driven flow regime, we fabricated 81 different samples under different combinations of inclination angle, sphere size, polystyrene concentration, and solution temperature; specifically, we used:

- Inclination angles of 20°, 45°, and 75°
- Sphere sizes of 500 nm, 1000 nm, and 2000 nm
- Temperatures of 2.9°C, 24.5°C, and 55.0°C. For this, the temperature of the solutions was controlled by placing the centrifuge tubes in water baths for over an hour. A hot bath was prepared with a beaker of water over a hot plate and its temperature was measured to be 55°C ± 1°C. A cold
bath was prepared with iced water and its temperature was measured to be $2.9^\circ\text{C} \pm 2.1^\circ\text{C}$. Room temperature solutions were used as prepared.

- Concentrations as given in Table 1. The concentrations were chosen such that there would not be significant sphere stacking.

<table>
<thead>
<tr>
<th>Sphere diameter (nm)</th>
<th>Colloidal concentrations (% v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.6, 0.9, 1.4</td>
</tr>
<tr>
<td>1000</td>
<td>1.0, 1.5, 2.3</td>
</tr>
<tr>
<td>2000</td>
<td>2.3, 3.5, 5.2</td>
</tr>
</tbody>
</table>

4.2 Optical validation

The prepared samples were characterized through optical microscope images with low magnification that allowed observation of large, representative areas of $\approx 1 \text{ mm}^2$ per image. Five microscope images were taken for each sample. In order to eliminate spatial variation effects intrinsic to this method, all images were taken across the horizontal centerline of the sample, avoiding the vicinity of the substrate edge, as those areas usually exhibited multilayer coverage due to solvent pinning near at the edge of the samples.

From the microscope images it was possible to observe differences of the substrate coverage as a function of the parameters that were varied in the experiments. We performed the self-assembly process for different combinations of inclination angle and solution temperature and we observed that these factors strongly influence the dynamics of the process and the resulting structures. Figure 10 shows representative microscope images of the structures obtained. We observed that at low solvent temperatures ($2.9^\circ\text{C}$) and high angles ($70^\circ$) the substrate was mostly uncovered with opals. As we increased the temperature, which in turn increased the evaporation rate, more spheres were left on the substrate after evaporation and the opal coverage on the substrate increases. The maximum coverage for a given angle always occurred at the highest temperature used of $55^\circ\text{C}$. Similarly, we observed that decreasing the angle of inclination increased the opal coverage of the substrate and the maximum coverage for a given temperature was obtained by using the lowest angle ($20^\circ$).
Figure 10. Opal coverage changes with solution temperature and angle of the substrate: Optical microscope images converted to greyscale of opals fabricated under different combinations of temperatures and angles for a colloidal concentration of 1.5% v/v and 1 µm spheres. As the angle of inclination of the substrate decreased, the opal coverage increased and as the solvent temperature increased, the opal coverage increased, both in agreement with our model. White areas correspond to no spheres present, black areas correspond to monolayer coverage, and gray parts correspond to multilayers. Scale bars are 200 µm.

The results shown in Figure 10 are in qualitative agreement with our proposed model: we observed that as the angle increases, the substrate coverage decreases in agreement with Equation 15. Also, as temperature increased, which in turn increases the evaporation rate, the coverage increased as also captured by Equation 15.

It should be noted that similar results had also been observed in literature, but have not been theoretically explained. In those studies, an intermediate angle was chosen to prevent both sphere stacking (at low angles) and empty parts of the substrate (at high angles). These studies also observed that a solvent that is more
volatile than water (and will therefore have a higher evaporation rate), like pure ethanol, leads to significant sphere stacking\(^ {59}\).

4.3 Image processing

To obtain a quantitative validation of the model developed, we performed image processing of the 81 different opals fabricated under the different parameters to obtain the coverage fractions of each sample.

The images were processed with a custom code that extracted the pixel intensity values. We used these values to categorize the image in three possible regions: (1) with no spheres, (2) with monolayer coverage, and (3) with sphere stacking as shown in Figure 11. The intensity threshold values between these regions were chosen to minimize the error by comparing with the original images.

![Figure 11. Representative image analysis process: (a) Light microscope image of the opal as obtained. (b) Processed image to show areas that have no spheres (in white) and areas that have spheres (black). (c) Processed image showing the parts of the sample with sphere stacking (gray). Scale bar is 200 µm.](image)

Based on the image processing, we then calculated the coverage fraction as

\[
\text{Coverage fraction} = \text{Pixel fraction}_{\text{coverage}} + \text{Pixel fraction}_{\text{stacking}},
\]

(21)

where \(\text{Pixel fraction}_{\text{coverage}}\) and \(\text{Pixel fraction}_{\text{stacking}}\) are the fraction of pixels that based on our defined thresholds were categorized as having spheres or multilayers, respectively. \(\text{Pixel fraction}_{\text{coverage}}\) corresponds to the black areas in Figure 11b and \(\text{Pixel fraction}_{\text{stacking}}\) corresponds to the gray areas in Figure 11c.
As implicitly assumed in Equation 21, in our image analysis we considered any stacking observed (Figure 11c) as corresponding to the presence of a second layer of spheres. This assumption was corroborated with our observation, using higher magnifications, that double layers are the dominant form of stacking for the relatively low values of colloidal concentration used in our experiments as seen in Figure 12.

![Figure 12](image)

**Figure 12.** Representative light microscope images showing regions of no coverage, monolayer coverage and multilayer coverage: We observed that for the parameters chosen, the opal samples would have (a) the three regions or (b) only monolayer, and multilayer coverage. When there were multilayers present, these were usually in the form of a second layer stacking on top of the first monolayer. Scale bar is 30 µm.

### 4.4 Comparison with model

The coverage fraction of each of sample was calculated by averaging the results from the five different microscope images taken at different locations for each of the 81 different opal samples fabricated. The resulting average coverage values are plotted in Figures 13, 14 and 15 for spheres of sizes 500 nm, 1000 nm, and 2000 nm, respectively, as a function of the parameter \( \frac{C}{1-C} \frac{(\sin \theta)^{-1/3}}{D} \), which is suggested from our model (see Equation 15).
Figure 13. Experimental results (circles) of the substrate fraction covered with opals formed at different inclination angles $\theta$, solvent temperatures, and colloidal concentrations $C$ for 500 nm spheres. Values higher than 1 represent multilayer coverage. Solid lines correspond to the model.

Figure 14. Experimental results (circles) of the substrate fraction covered with opals formed at different inclination angles $\theta$, solvent temperatures, and colloidal concentrations $C$ for 1000 nm spheres. Values higher than 1 represent multilayer coverage. Solid lines correspond to the model.
Figure 15. Experimental results (circles) of the substrate fraction covered with opals formed at different inclination angles $\theta$, solvent temperatures, and colloidal concentrations $C$ for 2000 nm spheres. Values higher than 1 represent multilayer coverage. Solid lines correspond to the model.

As shown in Figures 13, 14, and 15, the opal coverage increases with $\frac{C}{1 - C} \frac{(\sin \theta)^{-1/3}}{D} (1/\mu\text{m})$ for all sphere diameters, highlighting the role of these parameters in the self-assembly. In particular, it should be noted that this increase is linear for all the sphere sizes and temperatures studied, as seen by the match between the linear fits and experimental results, corroborating the validity of our proposed model in the gravity-driven flow regime (Equation 15).

Furthermore, the slopes of the best fit lines, which in our model are proportional to $\dot{m}''_{\text{evap}}^{1/3}$, increase with an increasing solution temperature used as shown in Figure 16, which is also in agreement with our proposed model.
4.5 Sources of error

Despite the very good agreement between model and experiments, it should be noted that there are some deviations from the model prediction in some of the coverage values obtained. This can be partially attributed to the simplicity of our model. For instance, in our model development, the evaporation flux was assumed constant and uniform. This would not be completely accurate in practice, especially for solutions at temperatures higher and lower than room conditions, due to distinct evaporation rates of the different solvents in the solution and heat transfer to the ambient which causes temperature variations in the solvents.

We attribute some of the differences between our model and the experimental results to be associated with this assumption. For instance, the samples formed from solutions at 2.9°C and 55.0 °C exhibited in general higher spatial variations of coverage along the sample. This result can be quantified by their coefficient of variation (see Table 2), defined as the ratio of the standard deviation to the average of samples prepared with the same combination of parameters, which was higher for samples prepared at high and low temperatures. This can be correlated to more pronounced spatial evaporation rate differences at those temperatures, which our model does not account for, and highlights the influence of the variation in the evaporation rate across the substrate.
Table 2. Coefficient of variation of the coverage fraction results obtained from image analysis

<table>
<thead>
<tr>
<th>Sphere size (nm)</th>
<th>Temperature (°C)</th>
<th>Coefficient of variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>2.9 ± 2.1</td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td>24.5 ± 0.9</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>55 ± 1</td>
<td>9.0</td>
</tr>
<tr>
<td>1000</td>
<td>2.9 ± 2.1</td>
<td>17.7</td>
</tr>
<tr>
<td></td>
<td>24.5 ± 0.9</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>55 ± 1</td>
<td>12.2</td>
</tr>
<tr>
<td>2000</td>
<td>2.9 ± 2.1</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
<td>24.5 ± 0.9</td>
<td>12.5</td>
</tr>
<tr>
<td></td>
<td>55 ± 1</td>
<td>15.7</td>
</tr>
</tbody>
</table>

We additionally observed some differences in the slopes of best fit for different sphere sizes at the same temperature as can be seen in Figure 16. We attribute this difference to small size-dependent effects that our model does not capture including particle inertial effects, which can lead to nonuniform concentrations, and flow deviations due to capillary attraction of particles, which in this regime where neglected.

4.6 Self-assembly of 10 μm particles

The dynamics of the self-assembly process were significantly different for the 10 μm particles compared to the ones described previously. Figure 17 shows representative time-lapse images of the self-assembly process for this sphere size. After the solution was drop-cast (Figure 17a), the spheres quickly attracted each other to form sphere clusters in the solution (Figure 17b). These clusters continued growing and simultaneously moved upwards (Figure 17c), against gravity, where they merged into each other to form a large polycrystalline sphere region. Spheres were continuously pulled to fill empty parts until eventually, when the solvents had fully evaporated, the substrate was fully covered with spheres (Figure 17d).
Figure 17. Time-lapse images of the self-assembly process on a 75° slope with a colloidal solution with 10 µm spheres. (a) The solution covered the substrate and the spheres were distributed in the solvent. (b) Spheres started to agglomerate in clusters (seen in white) due to capillary attraction forces. (c) The clusters became increasingly larger and were attracted upwards by capillary forces of spheres in the upper part of the substrate. (d) After all the solvents evaporated, the spheres formed a polycrystalline coating on the substrate.

These results can be interpreted in terms of the flotation forces and immersion forces discussed before (Figure 8). We attribute the initial formation of sphere clusters to the flotation forces between spheres, which due to the strong diameter dependence are negligible for spheres smaller than 10 µm. On the upper part of the substrate, where the film is thinnest, the liquid thickness will eventually drop below the sphere size generating immersion forces that pull more spheres upwards and leading to the formation of self-assembled arrays of spheres. We highlight that this immersion force has been shown to be relevant even for submicron spheres and in our experiments with particles of 500 nm - 2000 nm it has a role in the close-packing of the opals. However, due to its diameter dependence, it was more significant for the 10 µm spheres, changing the overall fluid and self-assembly dynamics. Additionally, since this force becomes relevant when the film thickness is smaller than the particle diameter, this force will act for longer times on bigger spheres, further contributing to the observed capillary effects for the 10 µm samples.
4.7 Summary

In this chapter we described the experimental validation performed to verify the accuracy of the model developed. In particular we performed experiments with different sphere sizes, colloidal concentrations, temperature of solvents, and inclination angles and performed image analysis to analyze the fabricated opals and quantitatively compare with our model. The results obtained show a good agreement with the model and show how the opal coverage can be controlled through the different parameters of the process in a rational way. We also noted how the dynamics will be of the self-assembly will be significantly different for larger spheres due to strong capillary forces, as we expected based on the theory.
Chapter 5

5. Rational fabrication of high coverage opals

Having validated our model for the slope self-assembly process, we leverage the insights obtained from this model to fabricate samples with an arbitrary sphere size in a simple, rational way. Due to the different physics acting for large and small spheres, as we have described previously, we performed fabrication of opals with spheres with diameters of 2 μm or less and with 10 μm spheres.

5.1 Opals with 2 μm or smaller particles

For sphere diameters below 2 μm, our model validation showed that the process will be governed by liquid drag and we can describe the substrate coverage with Equation 15. In particular, we can rewrite this equation as

\[
\text{Coverage fraction}_{\text{small spheres}} = a_{\text{sol}}(T) \left( \frac{1}{\sin \theta} \right)^{1/3} \frac{C}{(1 - C)D},
\]

(22)

where \(a_{\text{sol}}(T)\) is a constant that depends on the temperature and the properties of the solvents used.

Thus, by knowing how to reach the desired area coverage for a specific sphere size, which can be determined experimentally with the help of our model, and if the same solvents and temperatures are used, a similar coverage can be obtained for a different sphere size as long as concentration and angle are chosen such that the parameter \( \frac{C}{1-C} \left( \frac{\sin \theta}{D} \right)^{-1/3} \) is kept constant. Figures 18 and 19 show this process for 500 nm and 2000 nm spheres.

In those samples, we first determined the concentration that will yield a high monolayer coverage in one of the samples. To do this we started with a certain concentration and using our model (Equation 15 and Equation 22), we could determine the changes that we needed to do to either increase or decrease the coverage, depending on whether we had significant uncovered areas or sphere stacking, respectively. Then, the second concentration was chosen to have the same \( \frac{C}{(1-C)D} \) as the first sample since angle, solvents, and temperature were fixed.
Figure 18. 500 nm opal crystal with monolayer coverage: a) Light microscope image of a millimeter-scale opal which was achieved by tuning the self-assembly parameters with the aid of our model. b) SEM image of the opal structure. Sample was fabricated at room temperature, at a 45° angle, and with polystyrene concentration of 3.6% v/v. Opals obtained were ordered and polycrystalline and contained several defects like grain boundaries as seen in (a) and (b) and vacancies.

Figure 19. 2000 nm opal crystal with monolayer coverage: a) Light microscope image of a millimeter-scale opal which was achieved by tuning the self-assembly parameters with the aid of our model. b) SEM image of the opal structure. Sample was fabricated at room temperature, at a 45° angle, and with polystyrene concentration of 12.9% v/v. Opals obtained were ordered and polycrystalline and contained several defects like grain boundaries as seen in (a) and (b) and vacancies as can be seen by the bright spots in (a).

The samples demonstrated in Figures 18 and 19 have great promise due to their monolayer coverage over large (millimeter-scale) areas. Their area allows them to serve as templates for inverse opals to provide
hotspot cooling of electronics. By being monolayers, inverse opals formed with these templates would have the maximum permeability for a given thickness, compared to multilayered structures.

These templates are polycrystalline and contain several defects including cracks and vacancies, as can be seen in Figures 18 and 19 and as has also been observed with opals fabricated with other methods. In order to mitigate these defects, the insights generated from our model can be used to guide experiments to determine the temperatures, solvents, and angles that optimize crystallinity while maintaining large-scale area coverage.

5.2 Opals with 10 μm particles

We were also able to leverage the insights from our validated model to fabricate opals with larger sphere sizes where, as we described previously, the process is dominated by capillary forces. In particular, as shown in Figure 17, due to the strong sphere capillary forces against gravity, spheres do not tend to accumulate in the lower part of the substrate. Therefore, the minimum concentration to fully cover a substrate can be used to achieve large-scale, monolayer coverage. For an hexagonal packing, where the coverage fraction if there are no double layers or voids is \(~0.91\), we can use this value in Equation 20 to obtain the minimum concentration needed

\[ C_{\text{min}} = 0.91 \frac{2DA_{\text{sub}}}{3V_0}, \]  

where if a higher concentration is used, sphere stacking will occur and if a lower concentration is used, there will be uncovered parts of the substrate.

With this, we were able to fabricated opals with 10 μm pore sizes that had monolayer coverage as shown in Figure 20 using the concentration given by Equation 23.
Figure 20. 10 μm opal crystal with monolayer coverage: a) Light microscope image of a millimeter-scale opal which was achieved by using the concentration and volume of solution that our model suggested. b) SEM image of the opal structure. Sample was fabricated at room temperature, at a 75° angle, and with polystyrene concentration of 20.0% v/v. Opals obtained were ordered and polycrystalline and contained several defects like grain boundaries and vacancies.

Similar to the opals fabricated with smaller pore sizes (Figures 18 and 19), the 10 μm samples were polycrystalline and contained several defects. However, the samples had less prevalence of crack defects compared to previous work done with other methods that had cracks whose width was even larger than the sphere sizes.

It should be noted that in all the previous samples discussed before in Figures 18, 19, and 20, we were able to achieve monolayer coverage with little stacking and vacancies over a millimeter-scale area, which is a fraction of the total substrate area. The remaining areas of the substrate will still have significant coverage and larger areas of centimeter-scale length are possible (Figure 21a), but there will be more presence of sphere stacking and uncovered small patches in these areas.

We also explored the effect of the concentration used on the self-assembled structures made with 10 μm spheres. We observed, as shown in Figure 21b, that if the concentration used was less than the minimum value given for complete coverage given by Equation 23, the substrate will not be covered completely. Instead, the strong capillary forces pulled spheres to the upper part of the substrate and the edges, while the bottom remained uncovered since the spheres were depleted from the solution.
Figure 21. Centimeter scale opals on glass substrates fabricated using a) a volume of approximately 10 µL and 20% v/v concentration and b) approximately 12 µL and 10% v/v concentration. Both samples used 10 µm spheres and were fabricated at a 75° inclination and at room temperature.

5.3 Opals with 30 µm particles

To explore the limit of the slope self-assembly method, we attempted fabrication of opals with a diameter comparable to the average initial film thickness $h_0 \sim 25 \, \mu m$. Figure 22 shows representative SEM images of the structures obtained with spheres of 30 µm diameter. These structures exhibited significant non-close packed spheres and high non-uniformity in the coverage which makes them nonideal as a template for inverse opals.
Figure 22. SEM images of 30 μm colloidal spheres deposited with slope self-assembly method on a glass substrate. Spheres do not self-assemble into a close-packed and regular structure. Samples were fabricated with a colloidal concentration of 23% v/v at a 75° angle and at room temperature. Scale bar is 200 μm.

This behavior can be attributed to the fact that the spheres’ size is comparable to the film thickness. In this limit the spheres do not have significant time to move in the film under the action of capillary forces, since even from the start of the process a majority of the spheres protruded out of the film. In addition to the smaller effects of the self-assembly forces, larger spheres have higher inertia and therefore responded in a slower manner to applied forces, preventing them from assembling into an ordered structure in the short self-assembly time. These effects lead to the disordered and non-uniform coatings that can be seen in Figure 22.

We hypothesize that these effects can be mitigated by having larger initial thicknesses of film, which can be achieved by higher volumes of solution and by using substrates with higher contact angles with the solution used or by using solvents with smaller evaporation rates, as they will provide more time for the self-assembly process.
5.4 Opals in copper substrate

All the previous experiments were carried out in a glass substrate that proved optimal for the opal deposition process due to its low roughness and high wettability when treated with oxygen plasma, which facilitated the spreading of the colloidal solution in the substrate. However, in order to fabricate inverse opals via electroplating, as is traditionally done, it is necessary to have an electrically conductive substrate.

To demonstrate the possibility of carrying out the slope self-assembly method in different substrates which can be appropriate for electroplating, we also used mirror polished copper plate substrates. The copper plates were cleaned with ethanol, IPA, and acetone, dried with an air stream, cleaned in 1 M HCl for ≈5 minutes, dried with an argon stream, and plasma cleaned with argon plasma (5 minutes, 7 W). As it can be seen in Figure 23, in spite of the higher roughness and the lower wettability of copper (compared with glass), it was still possible to successfully apply this method in a copper substrate. This highlights the promise of this method in heat transfer applications, where copper is a commonly used substrate owing to its high thermal conductivity.

Figure 23. Opal deposition on copper substrate; a) centimeter-scale opal fabricated on a mirror-polished copper substrate. b) Light microscope image showing the opal monolayer formed. Spheres of 10 μm diameter were used.
5.5 Summary

In this chapter we demonstrated the successful fabrication of opals with sphere sizes ranging between 500 nm to 10 μm by leveraging the model that we developed. For the 500 nm – 2000 nm particles, we can control the angle of the substrate, the temperature, the solvents, and the colloidal concentration to fabricate opal monolayers, whereas for 10 μm particles we can control the volume and concentration used. We achieved monolayers in the millimeter-scale, while centimeter scale opals are possible with some sphere stacking or small uncovered areas.

We discussed the challenges with 30 μm particles which occur since the particle size approaches the thickness of the liquid film and we showed that this method can be applied to substrates that are more suited for inverse opal fabrication and heat transfer applications, like copper.
Chapter 6

6. Conclusions and Opportunities

6.1 Conclusions

This thesis presented a rational, controllable, and simple self-assembly method to fabricate opal structures with high throughput. We developed a scaling-based model of the slope self-assembly process to elucidate the relevant experimental parameters in the process which can be tuned to change the structures obtained and, in particular, control the opal coverage of the substrate. We performed experimental validation of the developed model with image processing and we confirmed its accuracy. We experimentally corroborated the existence of two regimes in the fabrication process: a gravity-driven flow regime for small spheres and a capillary-dominated regime for large spheres and provided guidelines to control the fabrication of structures in both of the regimes.

We successfully used the insights we obtained from our models to make opal templates with sphere sizes ranging from 500 nm to 10 μm with monolayer coverage over millimeter-scale areas. Even larger, centimeter-scale samples are possible with some sphere stacking or small uncovered areas. The structures that we fabricated, with pore sizes as high as 10 μm, with less prevalence of cracks, and being compatible with a copper substrate, have great promise in heat and fluid transport applications due to their potential for high permeability and intrinsic scalability.

6.2 Opportunities

From a fabrication perspective of the opals, future opportunities lie in the tailoring of the fabricated structures to the desired application. In this work, we demonstrated opals with pore sizes as high as 10 μm, which can yield significant gains in permeability over previously demonstrated inverse opals. However, we demonstrated that the method will eventually fail for even larger spheres due to the comparable sphere size and liquid film thickness. Future work can seek to expand the use of this method for larger sphere sizes, and therefore higher permeabilities, by experimenting with different contact angles between the substrate and the solution and by increasing the initial volume of solution used. Further model development can additionally elucidate the mechanisms of self-assembly of large particles to understand the roles of
increased particle inertia and effects of a film thickness comparable to the particle size. These modelling efforts can provide additional insights that enable the use of these method with even larger particles sizes, which could be relevant in electrochemical, gas evolution applications\textsuperscript{37}.

It also is necessary to understand the limitations of the structures that are fabricated with this method, including their crystalline defects, and how to mitigate them. By characterizing the fluid transport in the inverse opals that can be fabricated with the templating method that we have described, we can assess the deviations compared with an ideal, hexagonally packed structure and understand the role of the different defects in the overall fluid transport properties. With this knowledge, we can vary the different fabrication process parameters to minimize the most detrimental defects and therefore bridge the gap between ideal structures and our structures. This optimization should be done while also maintaining large-scale area coverage, which can be achieved with the models developed in this thesis.

In this work, we have focused on monolayer structures covering millimeter and centimeter-scale areas as these are significant for thermo-fluidic applications. Our insight and experiments can be used to expand the use of this method beyond these requirements. For instance, future work can seek to apply our developed model to control the number of layers in the resulting structure by leveraging the connection between coverage and number of layers. Additionally, future work should seek to expand this method to larger areas, which can allow the coating of large-scale heat transfer components in power generations plants, and to different substrate geometries, such as condenser tubes. This can be accomplished by exploring any effects that are dependent on the substrate geometry as well as by determining permissible ranges of roughness and curvature that would be compatible with this method.

Finally, the slope self-assembly method that we described can additionally be incorporated as part of more complex hierarchical fabrication processes. For instance, we can leverage our models on this method to fabricate structures that have more than one characteristic size, which can decouple viscous and capillary effects\textsuperscript{36} and therefore extend the performance of inverse opals in capillary-driven applications like condensation, thermal management, and pool boiling. Future work towards this goal should seek to understand the hierarchical structures that are accessible with our fabrication method as well as their quality and performance.
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