Architected Cellular Ceramics via Direct Foam Writing

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ARCHITEC TED CELLULAR CERAMICS VIA DIRECT FOAM WRITING

A dissertation presented by

by

JOSEPH THOMAS MUTH

to

The John A. Paulson School of Engineering and Applied Sciences

in partial fulfillment of the requirements

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Architected Cellular Ceramics via Direct Foam Writing

ABSTRACT

Cellular architectures are ubiquitous in nature due to their low density, excellent mechanical properties, and multifunctionality. The ability to create synthetic materials with similar architectural complexity would benefit several applications. Many manufacturing methods are unable to scalably replicate the cellular motifs present in natural structures, because they are either limited in build volume, restricted to photopolymerizable materials, or lack the requisite precision.

My Ph.D. thesis focuses on fabricating and characterizing architected cellular ceramics. Specifically, a new 3D printing technique is developed, referred to as direct foam writing, which enables the fabrication of hierarchically porous ceramics. Central to this technique is the design of a colloidal gel foam ink in which the continuous phase, an attractive alumina particle network, surrounds and interconnects dispersed bubbles. To formulate inks that satisfy the stability, microstructural, and rheological properties required for direct foam writing, we investigated the effects of several important parameters - surfactant concentration, surfactant hydrophobicity, pH, colloid volume fraction, and foaming intensity - on colloidal gel foam structure and elasticity. Notably, we identified a compositional range where colloidal gel foams display long term stability and high specific interfacial area. All stable foam compositions exhibited the desired rheology characteristics, i.e., solid-like behavior below a critical yield stress and shear thinning flow behavior, for direct writing. Moreover, we found that foam elasticity scales nearly linearly
with specific interfacial area for these colloidal gel foams.

We created ceramic architectures in the form of hexagonal and triangular honeycombs with closed-cell foam struts via direct foam writing. The sintered honeycombs have tailorable microstructure and geometry, programmable deformation modes, stiffness between 1.36 – 27.4 GPa, relative density as low as ~6%, and specific stiffness exceeding $10^7$ Pa/(kg/m$^3$). As an additional demonstration, we also produced 3D woodpile structures possessing filamentary features composed of a hollow core and porous cellular shell which are inspired by natural stem-like structures.

In summary, we developed and characterized colloidal gel foams which enable the direct writing of architected ceramics possessing multi-scale cellular features and exceptional specific stiffness. These materials may find application as lightweight structures, thermal insulation and tissue scaffolds.
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CHAPTER 1

INTRODUCTION

Hierarchical cellular architectures are pervasive in nature, e.g., wood [1], stems and quills [2], feathers [3, 4], bones [5], and others [3, 5], due to their exceptional mechanical properties and multi-functionality [5, 6]. Creating synthetic materials with similar hierarchical structures would be of significant interest for a broad array of applications including structural materials [5], catalysis [7], tissue engineering [8], and electrodes [9]. Despite increasing attention directed towards fabricating engineered cellular structures with multi-scale features, many limitations remain. Bulk foam processing techniques are capable of scalably producing large 3D objects composed of open or closed cellular microstructures. Depending on the fabrication method, the cell morphologies may be spherical [10], fractal-like [11], dendritic [12], or lamellar [13], among others [14], depending on the processing strategy. However, the bulk of foams are traditionally formed as simple monoliths [10, 15], that lack multi-scale cellular features. Conversely, light-based 3D printing is capable of producing architected matter possessing cellular features across multiple length scales [16, 17], but these techniques are limited to open cell constructs and are confined to photo-polymerizable resins which require some combination of post-fabrication coating and pyrolysis to form metallic or ceramic architectures [16–18]. Moreover, submicron resolution is required to pattern microscale cellular features via light-based 3D printing [16, 17], which often limits the overall build volume (< 1 mm³ [16]).

My Ph.D. dissertation focuses on combining the attributes of bulk foams and extrusion-based 3D printing to create large-scale, hierarchical cellular ceramics. Specifically, I have developed a new method, known as direct foam writing (DFW), to build mechanical metamaterials with macroscale honeycomb architecture and highly porous foam microstructure.
Towards this objective, foam inks with stable microstructures and predictable structure-elasticity evolution are developed, which possess the requisite viscoelastic properties required for direct writing [19–22]. After patterning and sintering, the foam microstructure retained within the struts of the printed honeycombs gives rise to enhanced mechanical properties compared to ceramic materials of comparable density.

1.1 DISSERTATION SCOPE

The first aim of my dissertation is to design a modular, foam ink with tailored stability, microstructure, and elasticity for DFW, an extrusion-based 3D printing method. The second aim is to use this foam ink to create hierarchical honeycombs with macroscale open hexagonal or triangular cells which are surrounded by closed-cell foam walls. The third aim is to characterize the elasticity of printed honeycombs composed of sintered foam and dense ceramic struts (as a control), and compare their specific stiffness to that reported for bulk foams and 3D lattices (i.e., octet trusses) made by light-based 3D printing.

The principal outcome of my Ph.D. dissertation is that direct foam writing enables the fabrication of a new class of hierarchical cellular materials, which are patterned by depositing colloidal gel foam (CGF) ink to produce macroscale honeycomb architectures with closed-cell porosity on the microscale. The foam ink is composed of a space-filling, attractive alumina particle network that surrounds and connects dispersed bubbles introduced via mechanical aeration. The stability, morphology, and elasticity of CGFs are investigated as a function of their composition, including surfactant concentration and hydrophobicity, pH, colloid volume fraction, and foaming intensity. By optimizing these parameters, highly stable (> 1 – 7 days) CGFs are created. Notably, within this stability region, the specific interfacial area (Σ) associated with the liquid-air interfaces can be tailored over two orders of magnitude. We also find that that
their shear elastic modulus scales nearly linearly with $\Sigma$ and that all stable CGFs possess the requisite viscoelastic behavior for DFW.

Hexagonal and triangular ceramic honeycombs with multi-scale cellular features are produced by DFW. The CGF microstructure is unaffected by the printing process, leading to sintered filaments with $>80\%$ porosity and $\sim$20-30 $\mu$m diameter pores, and honeycombs with a $\sim$6\% relative density compared to bulk alumina. By controlling their microstructure and nodal connectivity, we create ceramic honeycombs with varying deformation modes, stiffness values between 1.36 – 27.4 GPa, and higher specific stiffness ($>10^7$ Pa/(kg/m$^3$)) than either bulk alumina foams [23–25] or photopatterned octet trusses [26–28]. Lastly, we produce 3D woodpile materials composed of filaments with stem-like structural features to demonstrate the versatility of foam-based 3D printing.

1.2 DISSERTATION ORGANIZATION

In Chapter 2, relevant literature is reviewed on cellular solids theory, natural and engineered cellular materials, and the salient properties of colloidal gels, emulsions, and foams. In Chapter 3, the influence of CGF composition on foam stability, microstructure, and shear elastic modulus is reported. In Chapter 4, architected cellular ceramics are produced by direct foam writing, and their microstructure, elasticity, and specific stiffness are investigated. Finally, the conclusions of my Ph.D. are provided in Chapter 5.
CHAPTER 2  
LITERATURE REVIEW

2.1 MOTIVATION AND SCOPE

The ability to create ceramics composed of hierarchical cellular architectures may enable myriad applications, including lightweight structural materials, thermal insulation, tissue scaffolds, catalyst supports, and electrodes. In this chapter, prior research focused on architected cellular materials and ceramic foams is reviewed. First, we describe theoretical principles that govern the design of cellular solids along with examples of natural cellular architectures that exhibit optimized mechanical performance. Next, we discuss engineered cellular materials as well as the fabrication methods used to create them. Specific emphasis is given to direct ink writing and the structure-property relationships of colloidal gels and foams, which are the central focus of my thesis research.

2.2 MATERIALS SPACE AND CELLULAR SOLIDS THEORY

2.2.1 Defining Materials Space

Material space is the envelope of properties embodied by a particular material or group of materials. It is commonly visualized by creating an “Ashby Plot” [29], where different materials are compared based on two of their properties (Figure 2.1) [30]. Because material properties are numerous, a given plot represents a single two dimensional slice of the overall parameter space. This plot reveals unoccupied regions, i.e., corresponding to high modulus and low density, as well as low modulus and high density, that are inaccessible for fundamental reasons related to atomic size and bond strength [30]. Recent efforts have focused on expanding property space within accessible regions by creating engineered materials with novel architectures [16, 17, 22, 26, 28, 30–33].
Figure 2.1: Material space for (A) elastic modulus and density and (B) strength and density [30].
While traditional approaches for expanding material space, such as the development of new chemistries (e.g., alloy development, new ceramic and polymer compositions, etc.) and controlling microstructural features (e.g., phase distribution, grain size, defects etc.), are fruitful, they are no longer sufficient [30]. By contrast, manipulating architecture over multiple length scales offers a promising new approach to greatly expand material space [31]. Material architecture refers to the arrangement of multiple materials (including void space) on length scales that range from their microstructure to their overall geometric shape. Architected matter retains its classification as a “material” rather than a “structure” when perturbations are applied on length scales large enough for the material to respond as a continuum. Architectures of particular interest, include honeycombs (2D unit cell), lattices (3D unit cell), or foams (3D stochastic) (Figure 2.2) [31, 34]. The properties of these materials are dictated by the parent material and architecture.
Figure 2.2: Common unit cells for cellular solids. 2D periodic honeycombs with (A) triangular and (B) hexagonal cells. 3D periodic lattices with cells composed of (C) octet trusses and (D) tetrakaidecahedra. 3D stochastic foams with (E) closed and (F) open cells [27, 34, 35].

Consider the material space occupied by metals in Figure 2.1. Across all metal types and microstructures, elastic modulus ($E$) and density ($\rho$) range from $\sim 1 \times 10^0 - 4 \times 10^2$ GPa and $\sim 2 \times 10^3 - 2 \times 10^4$ kg/m$^3$, respectively. However, by introducing cellular architectures in the form of a 3D lattice or foam, the stiffness and density of aluminum, may be extended from $E \sim 2 \times 10^2 - 7 \times 10^1$ and $\rho \sim 2 \times 10^1 - 2 \times 10^3$ kg/m$^3$. Notably, this expansion of $E$ and $\rho$ is roughly 10x larger compared to the values of all bulk metals combined. If material architecture could be scalably manipulated to attain similar property space extension for other materials, significant advances in the performance of engineered materials may arise.
2.2.2 Characteristics of Cellular Solids

Cellular solids represent an important class of materials, for both natural and engineered systems [29, 36]. A given material is classified as a cellular solid when its structure consists of a connected network of struts or plates, and its density ($\rho^*$) compared to its bulk form ($\rho_s$) is less than 0.3, where $\rho^*/\rho_s$ denotes its relative density. For honeycombs and 3D lattices, relative density can also be expressed as a function of strut aspect ratio ($w/l$) where $w$ and $l$ are, respectively, the strut width and length and $C$ and $c$ are unit cell dependent constants [30]:

$$\frac{\rho^*}{\rho_s} = C \left(\frac{w}{l}\right)^c$$  \hspace{1cm} (2.1)

Similarly, the relative density of open and closed cell foams depend on $w/l$, except $w$ and $l$ refer to the thickness and side length of the plates composing the foam cells. The values of $C$ and $c$ for hexagonal and triangular honeycombs as well as foams are provided in Table 2.1 [30, 37].

**Table 2.1: Characteristics of common honeycombs and foams**

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>Deformation Mechanism</th>
<th>C</th>
<th>c</th>
<th>B</th>
<th>b</th>
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<td>Triangular</td>
<td>Stretching</td>
<td>$2\sqrt{3}$</td>
<td>1</td>
<td>1/3</td>
<td>1</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>Bending</td>
<td>$2/\sqrt{3}$</td>
<td>1</td>
<td>3/2</td>
<td>3</td>
</tr>
<tr>
<td>Foam</td>
<td>Bending</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

Cellular solids are broadly classified into two types based on their nodal connectivity. The effect of nodal connectivity manifests itself most readily in the mechanical response of the material. If the pin-jointed equivalent of the cellular solid collapses under applied load, then the real (i.e., fixed-jointed) cellular solid will deform primarily by bending of the struts. Conversely, if the pin-jointed material maintains its shape under load, then the primary deformation mechanism is stretching in the real material. For honeycombs and 3D lattices, the mechanical response can be determined *a priori* according to Maxwell’s rules for statically and
kinematically determinate frames (Equations 2.2 and 2.3, respectively) where $s$ is the number of struts and $j$ is the number of joints in a unit cell [37].

\begin{align*}
M &= s - 2j + 3 & (2.2) \\
M &= s - 3j + 6 & (2.3)
\end{align*}

When $M \geq 0$, the material is stretching dominated. However, when $M < 0$, the material is bending dominated. Using these rules, one finds that honeycombs with hexagonal and triangular cells are bending and stretching dominated structures, respectively. Open cell foams, along with closed cell foams that are characterized by thin walls and negligible gas pressure, also display bending character [37].

Nodal connectivity dictates the dependence of mechanical properties on relative density. As an example, the stiffness of a cellular solid ($E^*$) depends on relative density according to:

\[ \frac{E^*}{E_s} = B \left( \frac{\rho^*}{\rho_s} \right)^b \]  

(2.4)

where $E_s$ is the modulus of the parent material and $B$ and $b$ are unit cell dependent parameters given in Table 2.1 [30, 37]. The effect of nodal connectivity in terms of material space coverage is shown in Figure 2.1 for stretching dominated 3D lattices and bending dominated foams composed of carbon fiber reinforced polymer (CFRP) and aluminum [30]. Stretching dominated materials linearly decrease in stiffness as relative density decreases, while the stiffness of bending dominated materials decays more rapidly for equivalent relative density reductions. Hence stretching dominated materials are always stiffer compared to bending dominated ones at the same relative density. Equation 2.4 reveals the path to expanding material space via control over material architecture and relative density. Similar relationships exist for other mechanical properties, such as strength, but these are not discussed since this work focuses solely on stiffness.
Hierarchical cellular solids contain cellular features across multiple length scales. If the smallest characteristic “cells” exhibit the same mechanical response as the larger cells, then the mechanical response of either structure alone will be amplified. For example, a material with two levels of cellular architecture would exhibit bending-bending or stretching-stretching behavior. Conversely, mixed mode responses are observed when disparate nodal connectivities are combined (i.e., bending-stretching) [30]. The elastic modulus for a hierarchically cellular material is given by Equation 2.5 where 1, 2, n refer to the length scale of interest in order of increasing size and all other parameters have been previously defined [30]:

$$\frac{E^*}{E_s} = B_1 \left(\frac{\rho_2}{\rho_1}\right)^{b_1} B_2 \left(\frac{\rho_3}{\rho_2}\right)^{b_2} \ldots B_n \left(\frac{\rho_n}{\rho_{n-1}}\right)^{b_n}$$

Equation 2.5 suggests multi-scale cellular structures are uniquely suited to create ultra-low density materials with controllable mechanical responses. Consider a hypothetical cellular material containing two cellular length scales in which the largest length scale cellular structure (length scale = 2) is a hexagonal honeycomb \((B_2 = 3/2, b_2 = 3)\) with \(\left(\frac{\rho_2}{\rho_1}\right) = 0.2\). The struts of the honeycomb are also cellular (length scale = 1), and composed of foam \((B_1 = 1, b_1 = 2)\) with \(\left(\frac{\rho_1}{\rho_s}\right) = 0.2\). In this case, the overall relative density is \(\left(\frac{\rho_2}{\rho_1}\right) \left(\frac{\rho_2}{\rho_s}\right) = \frac{\rho_2}{\rho_s} = 0.04\) and the modulus of this material will be 0.05% of the bulk monolithic material. Thus, by varying material architecture from completely monolithic to first order cellular to n\(^{th}\) order cellular, one can expand \(E\) vs. \(\rho\) space from the bulk parent material to the architected structure, covering previously unattainable material space.
2.3 NATURAL AND ENGINEERED CELLULAR SOLIDS

2.3.1 Natural Cellular Solids

Nature is replete with examples of cellular solids, including wood [1], grass [2], cork [38], feathers [3], and bone [5], to name a few [6, 29, 36]. Importantly, these natural systems also possess multi-scale cellular features. Wood is perhaps the most common example of a hierarchical cellular solid. Its structure can be approximated as a hexagonal honeycomb with prismatic cells aligned along the major axis of the tree (with the grain direction) (Figure 2.3) [1, 2, 29]. The cell walls themselves are a multi-layered cellulose fiber reinforced matrix of hemicellulose and lignin. When loaded along the grain, the wood cells compress axially and behave as a stretching dominated structure. However, when loaded across the grain, the wood cells bend and the structure is bending dominated. Figure 2.4 shows the material space coverage for several common woods [1]. If the wood cell wall is considered alone, the moduli range is only ~10 - 60 GPa, and density is ~1500 kg/m³. However, its cellular architecture enables wood to span over one order of magnitude in density (~ 100 – 1000 kg/m³) and three orders of magnitude in stiffness (~0.02 – 20 GPa) [1]. If similar structures could be created from engineering materials, an analogous expansion of material space would occur.
Figure 2.3: Hierarchical architecture of wood. Cross-sectional images of wood (A) across the grain and (B) with the grain, highlighting wood’s honeycomb architecture [2]. (C) Schematic of the wood cell wall. The cell wall consists of multiple layers containing different orientations of cellulose fibers embedded in a lignin and hemicellulose matrix [1].

Figure 2.4: Elastic modulus vs. density material space for different types of wood [1].
The hierarchy found in natural systems also leads to improved mechanical performance. For example, stems and quills (hereafter referred to as natural stem-like materials) are high aspect ratio materials that resist axial self-loading as well as bending moments created by wind and other external loads [2, 39, 40]. From an engineering perspective, each of these materials can be approximated as a thin walled tube filled with a foam core interior (Figure 2.5) [2, 40]. The bending resistance of such a material is proportional to its shape factor ($\Psi$), where $\Psi$ depends on the second moment of inertia ($I$) and the cross-sectional area ($A$) according to:

$$\Psi = \left(\frac{4\pi I}{A^2}\right)$$  \hspace{1cm} (2.6)

For hollow circular cross-sections, this relationship reduces to the ratio of the tube radius ($a$) and the wall thickness ($t$). Thus, for thin walls and large radii, natural stem-like materials are incredibly efficient at resisting bending loads. However, for large radius to thickness ratios, local buckling (i.e., kinking) becomes the governing failure mechanism instead of bending [2]. In this scenario, the foam core prevents kinking by resisting ovalization of the global tubular structure, and by acting as an elastic foundation for the shell, while hardly adding any mass to the overall material. For example, a tube filled with a foam with relative density < 0.3 is far more resistant to buckling, in both axial loading and bending, relative to a tube of identical total mass and radius without a foam core (Figure 2.6) [2]. By manipulating material architecture across multiple length scales, stem-like materials are able to achieve enhanced functionality relative to materials without similar hierarchy.
Figure 2.5: Images of natural foam-filled stem-like materials including grass (A, B) and porcupine quills (C, D) [2, 40].

Figure 2.6: Mechanical performance of foam filled tubes. Plots of buckling resistance for (A) axial loading and (B) bending of foam-filled tubes relative to an empty tube at constant mass and radius as function of tube radius \((a)\) to wall thickness \((t)\) ratio [2].

Hierarchical natural cellular solids also enable additional functionality beyond mechanical stability. For instance, cork has a similar cellular structure to that of wood, except the cell wall material is much less rigid and its walls possess a series of corrugations (Figure 2.7) [38]. While its contribution to the overall stiffness of the tree’s trunk is negligible, its corrugated closed cell structure makes it extremely well suited to insulating the tree from heat, preventing
water loss, and protecting the tree from impact [29, 38]. Similarly, the foam structure within the rachus of bird feathers not only resists local buckling, but also often provides structural color [3, 4]. As a final example, the cellular structure of bone allows the skeleton to withstand complex loading conditions, while simultaneously facilitating fluid transport throughout the body [3, 5, 6].

Figure 2.7: Cork structure. (A) Schematic showing cork’s location in the tree. (B) The cork cells are oriented along the radial direction of the tree, perpendicular to the wood cells. Images of cork cells highlighting their (C) corrugated cell walls and (D) honeycomb structure (D) [38].

2.3.2 Engineered Cellular Solids

The natural architectures described above provide inspiration for engineered cellular solids. Through rational design, synthetic cellular materials have the potential to vastly increase materials space coverage, improve mechanical performance, and provide multi-functionality. Advances in any of these areas would have significant impact in applications ranging from
lightweight structural materials to tissue engineering scaffolds. To date, many engineered cellular solids have been produced from honeycombs, 3D lattices, and bulk foams, as discussed below.

2.3.2.1 Honeycombs

In the broadest sense, honeycombs denote any array of prismatic cells that pack in-plane to fill space (Figure 2.2A). The most common honeycombs are composed of hexagonal or triangular cells [29], although those with square [22], rhombic [41], or more exotic unit cells also exist [20, 42]. Because they possess regular geometry, their mechanical response is well predicted by analytical models, allowing their properties to be readily tuned by varying their unit cell geometry and relative density, as highlighted by Equations 2.1-2.4. Their mechanical properties can be in-plane isotropic or anisotropic depending on their unit cell geometry [29], but their out-of-plane properties are always distinct from their in-plane behavior due to their 2D structure. Traditionally, honeycombs are produced by die extrusion, stamping and joining, or casting [29]. However, recent advances in additive manufacturing (AM) have enabled honeycombs to be fabricated with unprecedented geometric flexibility and exceptional mechanical properties (Figure 2.8-2.9) [18, 22, 28].
Figure 2.8: Honeycombs. (A) Schematic of the stereolithography process, and images of the macro- and microstructures of SiOC honeycombs produced with this technique [18]. (B) The direct laser writing process and corresponding images of composite honeycombs (Scale bar: 10 µm) produced by depositing a ~ 50 nm thick coating of alumina on the printed polymer template [28]. (C) Schematic of direct ink writing of fiber reinforced epoxy ink, and images of the resulting hexagonal honeycombs (6 mm cell width), which possess anisotropically aligned fibers in the cell walls (Scale bar: 20 µm) [22].
Figure 2.9: Mechanical properties of honeycombs produced via additive manufacturing. (A) Compressive strength vs density for (A) SiOC honeycombs fabricated with stereolithography [18] and (B) ceramic-polymer composite honeycombs created with direct laser writing (honeycomb data circled in magenta) [28]. (C) Elastic modulus vs density space comparing fiber reinforced epoxy honeycombs printed with direct ink writing to balsa wood [22].
One AM technique used to produce honeycombs is stereolithography (SLA) [18]. In this method, a point source of UV light is rastered across a bath of photopolymerizable material (Figure 2.8A). The radiation penetrates to a depth fixed by the material and the radiation intensity, and locally crosslinks the exposed monomer at the focal point [18]. Alternatively, digital projection lithography (DPL) can be used to crosslink a planar slice via a reconfigurable photomask [26]. Subsequent layers are built up by immersing the cured layers into the bath of uncured resin in between radiation exposures. Because SLA and DPL are layer-by-layer, nearly arbitrary shapes can be created with feature sizes as small as 10 µm [26]. However, the materials palette is limited to photopolymerizable materials with additional chemistries only accessible through post fabrication deposition. Recently, SLA was used to create large area SiOC honeycombs from preceramic polymer resins (Figure 2.8A) [18]. In this case, defect-free solid features were formed since the photopolymerizable monomer was a direct precursor for the desired final material. However, preceramic polymers require pyrolyzation to form the final chemistry, which leads to large dimensional changes, and yields amorphous materials. Despite these challenges, ceramic honeycombs produced by this technique exhibited compressive strength $> 45$ MPa at a density $\sim 0.3$ g/cm$^3$, which corresponds to one of the highest specific strength values reported for cellular ceramic materials (Figure 2.9A) [18].

Direct laser writing (DLW) is another light-based patterning technique capable of producing honeycomb materials with excellent mechanical properties [28]. DLW leverages multi-photon adsorption to pattern photopolymers in a voxel-wise fashion (Figure 2.8B). A laser beam is precisely focused within a bath of transparent photopolymer, and polymerization only occurs at the focal point of the laser where two or more photons are absorbed. The focal point is optically translated throughout the build volume, allowing structures to be patterned with sub-
micron resolution, although build volumes are restricted to < 1 mm$^3$ [43]. Bauer et al. [28] employed DLW to produce shape-optimized composite micro-honeycombs with ceramic shells < 100 nm in thickness and polymer cores (Figure 2.8B). These honeycombs possessed anomalously high specific strength 0.25 MPa / (kg/m$^3$), the highest value among all existing natural and engineering materials with density < 1000 kg/m$^3$ (strength = 280 MPa, ρ = 810 kg/m$^3$) (Figure 2.9B) [28].

Direct ink writing (DIW) is a filament-based 3D printing technique in which a viscoelastic ink is extruded in concert with the prescribed motion of a translating gantry (Figure 2.8C) [22]. Importantly, patterning is controlled through ink rheology, rather than material chemistry. Inks are typically solid-like in the quiescent state, i.e., their shear elastic modulus ($G'$) exceeds their shear loss modulus ($G''$) for applied shear stresses below a critical yield stress ($τ_y$) (Figure 2.10). Above $τ_y$, the ink transitions to a liquid-like state, where $G'' > G'$. This behavior enables the ink to yield and flow in the nozzle (i.e., where the shear stress is high), but set immediately after exiting the nozzle (i.e., zero shear stress), to retain the desired filamentary shape. For sufficiently solid-like character, printed features may span gaps many times larger than the filament diameter (~1 µm – 1mm) [19]. Many materials including polymers [44], metals [21], ceramics [19], and others [45, 46] have been printed using this technique. Recently, Compton and Lewis created honeycombs composed of chopped fiber reinforced epoxy cell walls via DIW (Figure 2.8C) [22]. Notably, the fibers aligned along the print direction due to the shear stress within the nozzle. By integrating cell wall anisotropy within hexagonal and triangular honeycomb structures, engineered composites with specific stiffness akin to balsa wood were produced (Figure 2.9C) [22].
Figure 2.10: Schematic representation of viscoelastic behavior (blue) for inks employed in direct ink writing (DIW) compared to Newtonian fluids (red). Plots of (A) apparent viscosity as a function of shear rate and (B) shear moduli as function of shear stress.

2.3.2.2 3D Lattices

Lattices are characterized by space-filling 3D unit cells (Figure 2.2B). Like honeycombs, their unit cell shape and relative density determine their mechanical properties. The most common 3D lattice motifs are octet trusses (stretching dominated) [18, 26, 27, 32, 47], tetrakaidecahedron (bending dominated) [26], and woodpile structures (stretching or bending dominated) [19, 48–50] (Figure 2.2B, 2.11). In sharp contrast to honeycombs, isotropic mechanical behavior is possible for 3D lattices with isotropic unit cells. Moreover, the arrangement of struts in three dimensions allows one to create lower density materials compared to 2D cell structures [26, 27, 32]. Due to their geometric complexity, 3D lattices are commonly constructed using AM.
Figure 2.11: Woodpile lattices. (A) Woodpile lattice scheme. (B) Images of woodpile materials with (B) simple cubic (SC) and (C) face-centered tetragonal symmetry (FCT), at 0% compressive strain (top row) and 25% compressive strain (bottom row) (Scale bars: 500 µm). These images coupled with the compressive stress vs. compressive strain plot shown in (D) depict stretching deformation mechanisms in SC woodpiles and bending deformation mechanisms in FCT woodpiles [48].

Light-based AM methods, such as DPL [26] and DLW [27, 28], have been used to create 3D lattices, including polymeric, metallic, and ceramic octet trusses and tetrakaidecahedra with
stiffness ranging from $1 \times 10^6 - 3 \times 10^9$ Pa and $3 \times 10^6 - 1 \times 10^9$ Pa and densities between $\sim 7 \times 10^1 - 3 \times 10^2$ kg/m$^3$ and $5 \times 10^0 - 3 \times 10^2$ kg/m$^3$, respectively (Figure 2.12-2.13). Another photopolymerization technique, self-propagating waveguide polymerization (SPWP), is also capable of fabricating 3D lattices (Figure 2.12) [18, 32, 51]. SPWP uses collimated UV light in conjunction with a two-dimensional photo-mask and a bath of suitable photo-curable monomer to produce 3D lattices. When the UV radiation is incident on the surface of the monomer bath, the monomer polymerizes and acts as a waveguide that allows the UV light to penetrate into the bath a fixed angle and cure material throughout the depth of the bath. SPWP has been used to create octet trusses composed of hollow nickel tubes hundreds of microns in diameter and possessing wall thicknesses as thin as $\sim 1$ nm (Figure 2.12) [32]. As a result of their architecture and thin strut walls, these 3D lattices achieved recoverable compressive strains up to 50%, and stiffness and density ranges spanning three and two orders of magnitude, respectively (Figure 2.13C). However, the SPWP technique is restricted to creating 3D lattices with linear features, and printed features $> 10^2 - 10^3$ µm. Also, this technique is restricted to photopolymers, and therefore, requires post-fabrication deposition or coating to transform the printed architectures into metal or ceramic lattices.
Figure 2.12: 3D Lattices. (A) Images of 3D lattices produced with digital projection lithography including (from left to right) solid polymer, hollow metallic, and hollow and solid ceramic specimens [26]. (B) Images of ceramic-polymer composite 3D lattices (Scale bars: 10 μm) and an octet truss with hollow ceramic struts fabricated with direct laser writing [27, 28]. (C) Schematic of the self-propagating waveguide polymerization technique and images of an example printed polymer template and the corresponding nickel lattice [32].
Figure 2.13: Elastic modulus vs density materials space coverage for 3D lattice materials created by light-based 3D printing techniques. (A) Digital projection lithography (red, blue, and green data) [26], (B) direct laser writing (orange and purple data) [27], and (C) self-propagating waveguide polymerization (black squares) [32].
While DIW cannot produce 3D lattice unit cells with out-of-plane spanning features, it is well-suited to produce woodpile architectures [19, 48, 49]. Woodpiles consist of layers of parallel filaments, where the interfilament spacing and layer orientation can be varied (Figure 2.11). By tailoring their architecture, materials with simple cubic [48], face centered tetragonal [48], or other geometries may be created [19]. While these lattices neither replicate the mechanical efficiency of octet trusses, nor the ideal bending behavior of tetrakaidecadra, they exhibit properties between these two extremes, and may also possess anomalous characteristics, such as negative stiffness [48, 49].

Up to this point, all engineered honeycombs and lattices that have been discussed contain a cellular motif on a single length scale. However, as mentioned in 2.2.2, materials with cellular motifs on multiple length scales have added performance and material space benefits compared to materials without cellular hierarchy. Greer et al. [16] created the first synthetic multi-scale cellular material by employing DLW to create ceramic octet trusses composed of octahedral unit cells over three different length scales (Figure 2.14). These materials display unprecedented $E$ vs. $\rho$ material space coverage, spanning nearly three orders of magnitude in density and two orders of magnitude in stiffness, while maintaining relative density between $\sim 10^{-1}$-$10^{-4}$ (Figure 2.15) [16]. Furthermore, these architectures were able to recover 85-98% of their original shape for compressive strains $> 50\%$. Their exceptional resilience was attributed to their self-similar design and submicron feature size.
Figure 2.14: Multi-scale octet truss produced by direct laser writing that possesses struts composed of octets across three length scales [16]. (Scale bars: (A) - (E): 20 µm, (F): 50 µm, (G): 10 µm, (H): 25 µm)
Figure 2.15: Mechanical properties of multi-scale cellular materials. Plots of (A) elastic modulus vs. density material space for hierarchical octet trusses produced via direct laser writing [16], and (B) specific strength vs. tensile strain for multi-scale materials fabricated with large area projection microstereolithography (orange data) [17].
Spadaccini et al. [17] created similarly complex architectures by designing a new light-based 3D printing technique called large area projection microstereolithography (LAPM) in which direct laser writing and stereolithography are integrated in the same platform (Figure 2.16). Importantly, this technique is capable of integrating cellular features across multiple length scales (four layers of cellular features spanning six orders of magnitude in length scale), while maintaining large build volume (> $10^3$ mm$^3$). Such unprecedented control of material assembly affords an exceptionally wide range of programmable deformation mechanisms and resilience. Specifically, by tuning cellular structure at each length scale they observed 100% elastic recovery at tensile strains > 20% for a variety of different hierarchical cellular schemes (Figure 2.15). These prior studies have begun to unlock the potential of high performance multi-scale cellular solids as structural metamaterials. However, they remain limited to UV polymerizable materials and, with the exception of LAPM, to small build volumes [16].
Figure 2.16: Multiscale octet truss fabricated by large area projection microstereolithography (LAPM). Schematic of the LAPM process and images of a representative material produced using this technique. LAPM enables large scale fabrication of hierarchical architectures with cellular features spanning six orders of magnitude [17].

2.3.2.3 Bulk Foams

While AM technologies are well suited to programmably define material architecture, prescribing microstructural features with a top-down approach limits process scalability and
restricts the range of achievable material chemistries. By contrast, bulk foaming techniques are well suited at efficiently producing micro-scale features over large volumes, but inherently lack the control necessary to produce multi-scale hierarchical materials [15]. By combining the microstructural length scale control produced by foaming with the material placement capability afforded by DIW, one could scalably produce new classes of hierarchical cellular materials. Here, we review the properties of foams as well as techniques for producing macroporous ceramics with the goal of identifying a processing regime compatible with DIW.

A foam’s pore structure influences its mechanical behavior and applications [29]. If the solid from which the foam is made of is confined to the cell edges, and neighboring cells abut through open faces, it is considered an open cell foam. Conversely, if adjoining cells are sealed off from each other by solid faces of material, the foam is closed-celled. Open cell foams deform by cell-edge bending and have stiffness given by Equation 2.4 [29]. Closed cell foams have an additional stiffness contribution from the combined stretching and bending of the cell faces. The stiffness of closed cell foams is given by Equation 2.7, where $C_1$ and $C_1'$ are experimentally determined proportionality constants and $\phi$ is the volume fraction of the solid contained in the cell edges [29].

$$\frac{E^*}{E_s} = C_1 \phi \left(\frac{\rho^*}{\rho_s}\right)^2 + C_1' (1 - \phi) \left(\frac{\rho^*}{\rho_s}\right) \tag{2.7}$$

In some cases, the pressure of the entrapped gas in closed cell foams may further increase stiffness, but this contribution is typically negligible for ceramic materials, since the solid modulus is high and the failure strain is low [37]. Many foams fall between purely open and strictly closed morphologies. Hence, the foam mechanics proposed above should be viewed as bounds for material behavior, where microstructures that are more closed tend towards the stiffer limit, while more open microstructures approach the open cell lower bound. Besides affecting
mechanics, cell structure also frequently dictates a foam’s application. Open cell foams are typically employed when fluid flow through the material is important (e.g., filtration, catalysis, charge exchange), while closed cell foams are better suited to applications where mechanical or thermal properties are paramount [29, 36].

Ceramic foams are of interest for a variety technical applications, including lightweight structural materials [5, 33], catalyst supports [7], high temperature filtration [52], insulation [53], battery electrodes [9], tissue scaffolds [8], and others [54]. Coupling inherently porous ceramics with globally cellular architectures would be especially interesting not only for further exploration of materials space, but also for attaining many of the above mentioned functionalities within the same material. With these applications in mind, we focus on reviewing bulk processing techniques for creating macroporous ceramics. We use “macroporous” as defined according to the IUPAC definition, which stipulates that the material contain greater than 50% void volume and possess nominal pore diameters exceeding 50 nm [55]. This guideline eliminates techniques like partial sintering and solid state pore formation (low void volume and poor robustness), sol gel methods (excessively small pore size), and other methods that produce porous ceramics [14].

Several techniques have been developed to produce macroporous ceramic foams, including replication, sacrificial templating, capillary suspensions, and direct foaming (Figure 2.17) [11, 14]. In replication, a sacrificial material is used as a positive replica for the final ceramic part (Figure 2.17A) [56]. The sacrificial material is infiltrated or coated with the ceramic precursor, which is then dried or set such that it can hold its shape. Next, the template is removed by pyrolysis, dissolution, or leaching. Finally, the precursor is densified to form the final ceramic
part [56, 57]. This technique is restricted to forming open porous materials and requires a pre-existing template, precluding the development of multi-scale cellular materials.
Figure 2.17: Macroporous ceramic foams. Processing schemes for (A) replication [56], (B) sacrificial templating [58], (C) capillary suspensions [11], and (D) direct foaming and representative images of sintered ceramic microstructures formed by each technique [59].
Sacrificial templating utilizes a negative template to impart the desired microstructure to the ceramic [14]. Typically, a multi-phase suspension or powder mixture is prepared in which one or more of the phases act as a fugitive material (Figure 2.17B) [56]. Once the precursor is set in the desired shape, the fugitive is removed, and the continuous phase is densified, leaving behind a negative replica of the sacrificial material in the final part. Liquid or solid porogens may be used, and the resulting microstructures can be open or closed depending on the connectivity of the porogen. However, for sufficiently large parts with high fugitive content (> 20 vol%), the removal of the sacrificial material may require long times or cause cracking [60, 61]. To minimize defects resulting from porogen removal, techniques such as freeze casting use liquid pore formers or easily sublimated solids [12, 62–64].

Capillary suspensions offer an alternative approach, in which particles are initially dispersed in a non-wetting fluid (Figure 2.17C). Upon introduction of small amounts of a wetting fluid (< 1 vol%), interstitial bridges of the wetting fluid form between the dispersed particles, binding the particles together via capillary attraction and arresting the particle network [65]. The suspension is then dried and sintered, forming a porous ceramic with pore structure determined by the interstitial volume within the particle network. The final pore network is open, which facilitates fluid flow [66, 67]. The pores themselves are similar in size to the dispersed particles, and the pore boundaries are determined by interparticle necks that form during sintering [25, 68, 69]. However, as a result, these ceramics have comparatively poor mechanical characteristics relative to what is expected based on their relative density and cellular solids theory [25].

2.3.2.4 Direct Foaming

In direct foaming, air is incorporated into a colloidal suspension or precursor solution by mechanical (e.g., frothing) or chemical (e.g., blowing agents or gas generating reactions)
methods [14]. After aeration, the foam is cast into the desired shape and then sintered to yield closed cell porous ceramic (Figure 2.17D). In this technique, no porogen removal is required. As such, nearly defect-free ceramics with porosities up to 97 % [70] and pore sizes from \( \sim 10^1 \)-\( 10^3 \) µm can be formed [14, 71]. However, wet foams are energetically unstable due to their excess interfacial area. Thus, significant structural degradation may occur prior to solidification, e.g., creaming, coalescence, and Ostwald ripening, if the entrained bubble interfaces are not well stabilized.

Creaming occurs when the entrained air physically separates from the continuous phase, creating an upper region of liquid-poor material, and a lower region of liquid-rich material. During this process, the continuous phase continuously drains through the interconnected network of low-pressure regions at the plateau borders of bubble triple junctions. Once sufficient drainage occurs such that neighboring bubble interfaces are brought in close proximity, the negative disjoining pressure in the continuous lamella causes the thin films to rupture, and the bubbles to coalesce.

Ostwald ripening occurs due to the pressure gradient arising between neighboring bubbles of different radii. The gas pressure inside a bubble is governed by the bubble’s Laplace pressure. For spherical bubbles, the Laplace pressure is expressed by Equation 2.8, where \( \Delta P \) is the pressure difference between the inside and outside of the bubble, \( \sigma \) is the surface tension and \( r \) is the bubble radius.

\[
\Delta P = \frac{2\sigma}{r} \tag{2.8}
\]

When a smaller bubble is in contact with a larger bubble, gas will diffuse from the small bubble into the large bubble causing disproportionation.
Drainage and coalesce can be mitigated by increasing the viscosity of the continuous phase to kinetically arrest creaming or by attaching long chain surfactants to the bubble interfaces to sterically hinder coalescence. However, neither of these stability mechanisms prevent Ostwald ripening [14]. As a result, wet foams may destabilize within ~seconds to minutes after formation. However, colloidal particles that spontaneously and irreversibly attach to liquid-gas interfaces have been shown to successfully stabilize foams for ~days – weeks without signs of structural degradation (Figure 2.18) [72, 73]. Similar observations exist for Pickering emulsions, where solid particles permanently stabilize interfaces separating hydrophobic and hydrophilic phases [74–77]. The permanent attachment of these particles is driven by their surface energy and their size. When air is entrained in the suspension, high energy liquid-gas interface is introduced. If the solid-gas interfacial energy is intermediate that of the solid-liquid and the liquid-gas interfacial energies, the particles will spontaneously attach at the liquid-gas interface (Figure 2.19). Suspension conditions favoring particle adsorption are attained by either adjusting the particle’s hydrophobicity by attaching short chain surfactants [73, 78] or by using co-solvent mixtures to tune the liquid surface tension [79, 80]. The position of the particle on the interface is defined by its contact angle (θ) with the continuous phase. The attachment energy (E) associated with particle adsorption (i.e., the energy savings associated by attaching a particle on the interface versus the pure liquid-gas interface) is given by Equation 2.9, where \( r \) is the particle radius is \( \sigma_{lg} \) is the interfacial energy of the liquid-gas interface, and \( \cos \theta \) is negative for \( \theta < 90^\circ \) (i.e., for foams) and positive for \( \theta > 90^\circ \) (i.e., for mists) [76].

\[
E = \pi r^2 \sigma_{lg} (1 \pm \cos \theta)^2
\]  

Hence, for larger contact angles, particle attachment is more favorable. Larger particles are also able to stabilize more area per particle, producing stronger attachment energies. However, in the
limit of excessively large particle sizes, gravity dominates particle mobility, destabilizing the system. Attachment energies as function of contact angle and particle size are shown in Figure 2.18B. Notably, for contact angles ranging between 20° - 90°, attachment energies for colloidal particles span ~10^2 – 10^6 kT (where k is the Boltzmann constant, and T is absolute temperature), compared to ~10^0 kT typical for amphiphilic surfactants [81]. Particle attachment is irreversible, thereby serving as a steric barrier to coalescence. Moreover, particles in these systems frequently have strong attractive interparticle interactions, leading to the formation of a nearly close-packed particle array on the bubble interface [82, 83]. The particle array allows the bubbles to maintain their shape and resist Ostwald ripening for long time periods.

**Figure 2.18: Stability of particle-stabilized foams.** (A) Plot of average bubble size as a function of time for conventional surfactant stabilized foams (shaving foam) compared to systems stabilized by particles functionalized with short chain surfactants [59]. (B) Plot of energy of attachment as a function of contact angle for different sizes of particles. The higher adsorption energy of particles on liquid-gas interfaces compared to surfactants makes solid stabilized foams far more stable compared to surfactant stabilized foams.
Figure 2.19: Particle adsorption at liquid gas interfaces. (A) When the wettability of dispersed particles is intermediate that of the pure gas and the pure liquid, the equilibrium position of the particles is at the liquid-gas interface [79]. Under these conditions, particles will spontaneously and irreversibly adsorb on the liquid gas interface upon aeration of the suspension (B) [72].

Particle stabilization of foams is dependent solely on particle size, shape, and hydrophobicity. It is therefore possible to use many types of particles, including ceramics [84–86], metals [87, 88] and polymers [79, 80]. Through careful formulation, multiple particle populations may act as stabilizers in a given system [89, 90]. By independently tailoring the energy of each particle type, foams can be stabilized completely by one particle population or the other, or by mixtures of both types [90]. When both particles act as stabilizers, open cell foams can be created if one of the particle population serves as a porogen (Figure 2.20) [90].
Figure 2.20: Multi-particle adsorption on liquid-gas interfaces. Processing map for producing particle-stabilized foams in which there are two or more particle populations. Depending on particle wettability and concentration, the foam can be entirely stabilized by one population while the non-adsorbing phase remains dispersed, or both particle types can participate in stabilization [90].

Due to their highly stable nature, particle-stabilized foams do not require a setting step after formation, and thus, can be dried and sintered without microstructural degradation [91]. Sintered particle-stabilized foams may possess cell walls that are composed of a single grain, in thickness, while possessing porosity above 80% [33, 70]. Closed cells coupled with thin cell walls and close-packed spheroidal or polyhedral cell shapes, enable final architectures to achieve mechanical properties near their theoretical limit [33]. Importantly, their mechanical properties are frequently superior compared to porous ceramics produced by sacrificial templating or
capillary suspensions, since these methods produce open cells with angular features that act as stress concentrators [33]. To date, both closed and open cell particle-stabilized foams have been used to create bulk structural materials [15, 23, 92] and tissue scaffolds [93, 94], respectively.

2.4 STRUCTURE - ELASTICITY RELATIONSHIPS OF COLLOIDAL GELS AND FOAMS

Particle-stabilized foams consist of air dispersed within a continuous phase composed of a colloidal gel. Particle stabilization has also been well documented in emulsions containing Newtonian fluids (Pickering emulsions) [74–77]. However, we are interested in a new class of foams, referred to as colloidal gel foams (CGFs). To better understand this nascent system, we first introduce the microstructure-elasticity relationships for pure colloidal gels, particle-free dispersed systems (i.e., conventional fluid foams and emulsions), and particle-stabilized dispersed systems (i.e., Pickering emulsions and their derivatives). Each of these systems is discussed in the remaining sub-sections.

2.4.1 Colloidal Gels

Colloidal gelation ensues when attractive interactions between particles leads to the formation of a space-filling network that has finite elasticity [95]. Attractive interparticle interaction may arise from low particle surface charge [96], screened electrostatic repulsion [97], depletion interactions [98, 99], polymer bridging [100], or changes in solvent quality [101, 102]. For sufficiently strong attractions, network formation can completely arrest particle motion in the system. When flocculation occurs in systems where the colloid volume fraction (φ_c) is below the gelation volume fraction (φ_gel), particles aggregate into low density, fractal-like clusters [102–105]. Percolation theory has been shown to accurately predict the onset of gelation (i.e., when the clusters connect to fill space) and subsequent scaling of the system’s elasticity [103–105].
Fractal structure is central to percolation theory models. The fractal cluster size ($\xi$) can be estimated by Equation 2.10, where $d$ is the particle size, $\phi_{rcp}$ is the random close packing volume fraction, and $D$ ranges between 1.75 - 2.2 depending on the aggregation mechanism [106].

$$\frac{\xi}{d} = \left(\frac{\phi_c}{\phi_{rcp}}\right)^{\frac{1}{D-3}} \quad (2.10)$$

Thus, for attractive interparticle interactions and low $\phi_c$, sample spanning networks readily form since the average floc size is large. However, as particle volume fraction increases, gelation is dominated by particle-particle aggregation, rather than cluster-cluster interactions. As an example, for a suspension with $\phi_c = 0.35$, the characteristic cluster size is ~1-2 particle diameters. Hence, percolation theory no longer describes the system’s behavior [105]. Above this limit, the gel structure is more closely approximated as weakly connected, dense particle clusters separated by heterogeneous voids [95, 101, 107].

Gelation leads to pronounced rheological changes, as shown in Figure 2.10. Colloidal gels exhibit solid-like behavior below $\tau_y$, where $G'$ is frequency independent and exceeds $G''$. Above $\tau_y$, the particle network is disrupted, and fluid-like behavior is recovered. $G'$ and $\tau_y$ both display power law scaling with $\phi_c$ (Figure 2.21) [108]. For systems in the fractal regime, scaling exponents between 3 and 5 are typical [104]. Power law scaling of the elastic properties is still observed outside percolation theory bounds, but the scaling exponents can be larger [95, 107].
Figure 2.21: Elastic properties of colloidal gels. (A) Plot of shear elastic modulus as function of frequency for colloidal gels with different solids contents. Plots showing the power-law scaling of (B) shear elastic modulus and (C) shear yield stress as a function of solids content for colloidal gels created at different suspension pH values [108].
2.4.2 Particle-free Foams and Emulsions

From a structural and rheological viewpoint, fluid foams and emulsions behave identically. Therefore, we will collectively refer to them as “dispersed systems.” In the absence of particles, dispersed systems are typically characterized by two or more fluid phases, in which one or more of the fluid phases are dispersed in an immiscible continuous fluid. (For foams, the dispersed fluid is air.) For repulsive interactions between dispersed phase entities, there is no network formation, and therefore negligible elasticity, when the volume fraction of the dispersed phase ($\phi_b$) is below $\phi_{rcp}$ (Figure 2.22) [109–111]. As the dispersed system is compressed beyond $\phi_{rcp}$, the dispersed phase deviates from sphericity, and stores excess elastic energy in its interface. The amount of energy stored in the interface is proportional to the Laplace pressure of the system [110, 111]. Moreover, because the dispersed phase entities now form a continuous network, the system transitions to a gelled state. Beyond the gelation threshold, the elasticity of the system is a function of the Laplace pressure ($\sigma/r$), and the volume fraction of dispersed phase beyond $\phi_{rcp}$ (Equation 2.11) [110, 111].

\[ G' \sim \frac{\sigma}{r} \phi_b (\phi_b - \phi_{rcp}) \]  

(2.11)

In prior work, Derjaguin and Wilson showed that in the dry limit (i.e., $\phi_b = 1$), elasticity is given by Equation 2.12, and solely determined by the surface tension and specific interfacial area ($S/V$, where $S$ is the interfacial area and $V$ and is the sample volume) [112, 113]. Both equations suggest that all of the elasticity in dispersed systems is related to the density of interfaces and the energy associated with each interface.

\[ G' \sim \sigma \frac{S}{V} \]  

(2.12)
Figure 2.22: Elastic properties of repulsive and attractive emulsions. Plots of shear elastic (filled symbols) and loss moduli (open symbols) as a function of frequency for (A) repulsive and (B) attractive emulsions. (C) Plot of shear moduli as a function of dispersed phase fraction for repulsive (diamonds, and down-pointing triangles) and attractive (squares and up-pointing triangles). The elasticity of attractive emulsions persists below close packing, whereas repulsive systems are only elastic above close packing [109].
Similar behavior is observed for attractive dispersed systems. However, in this case, gel-like behavior is observed well below close-packing of the dispersed phase since a network can form before interfacial distortion occurs [109]. These systems exhibit similar structures and rheology to colloidal gels, except the volume fraction of the dispersed phase replaces the volume fraction of colloidal particles in the analysis. When the dispersed phase volume fraction exceeds close packing, Laplace pressure contributions add to the elastic response (Figure 2.22) [109].

2.4.3 Particle-stabilized Dispersed Systems

Particle-stabilized dispersed systems have additional energy storage mechanisms compared to their particle-free counterparts that may act at the dispersed phase interface [82, 83, 114] or throughout the continuous phase (network mechanisms) [115–118]. As shown in Figure 2.19, the thermodynamically favorable position for particles with intermediate wettability, is on the dispersed phase interface. Thus, as interfacial area is introduced, particles pack tightly on the interface and form an armor-like shell [34, 82, 83]. When all of the particles in the system are located on interfaces, the elasticity of the armor layer dominates the bulk elastic response [82, 83]. For interfacial areas typical of most dispersed systems, this corresponds to $\phi_c \sim 0.0001$–0.01 [119]. For repulsive interparticle interactions, the structure-elasticity relationship is exactly analogous to repulsive particle-free systems, except the interfacial elasticity dictates the Laplace scaling instead of the surface tension [82, 83]. Attractive systems not only have stronger armor layers, but also percolate when $\phi_0 < \phi_{rcp}$ (Figure 2.23). In this scenario, elasticity follows the theory developed for colloidal gels [83, 114]. Above close packing, the elasticity of the armor-like interfacial layer also contributes to the bulk elastic response (Figure 2.23) [82, 83].
Figure 2.23: Elasticity of emulsions stabilized by interfacially adsorbed particles. Plots of shear moduli as a function of (A) shear strain and (B) frequency, for particle-stabilized emulsions at different dispersed phase fractions. (C) Plot showing the scaling of the shear elastic modulus with Laplace pressure and dispersed phase fraction compared to data collected for particle-free repulsive emulsions (solid line). All plots correspond to particle-stabilized emulsions where all of the particles are adsorbed on interfaces [83].
When $\phi_c$ exceeds the value necessary for interfacial stabilization, excess (non-adsorbed) particles may aggregate into flocs themselves, forming a gel that bridges neighboring dispersed phase entities [117, 118, 120–122]. This behavior further increases the elastic response of the system and accelerates the transition to a bulk gel. Sometimes, as the strength of the colloidal gel in the continuous phase increases, the armor layer surrounding the dispersed phase may be disrupted (Figure 2.24) [118]. However, the dispersed phase remains stable. It has been hypothesized that the network of particulate flocs is sufficiently strong to arrest dispersed phase movement, preventing creaming [118]. Because the bubbles are separated by the network, coalesce is eliminated and minimal Ostwald ripening is observed, even though portions of the interface remain uncovered. Despite the ubiquity of particle-stabilized systems formulated with $\phi_c$ in this regime [10, 80, 87], no structure-elasticity scaling laws have been developed to date.
Figure 2.24: Elasticity differences between interfacial and network stabilizing mechanisms. (A) Image of the dry microstructure of a particle-stabilized emulsion containing silica particles that act as interfacial stabilizers and chitosan macromolecules that impart network stabilization. Shear moduli for the same emulsions for different chitosan contents as a function of (B) strain and (C) time as determined by bulk and interfacial rheometry, respectively. At low chitosan concentration, the bulk and interfacial measurements exhibit substantial elasticity, whereas at high chitosan concentration, only bulk elasticity is present – indicating that interfacial stabilization is disrupted [118].
Structure-elasticity relationships are even less well understood in particle-stabilized dispersed systems when the continuous phase possesses sufficiently high $\phi_c$ such that it is gelled far beyond the percolation threshold, i.e., where CGFs are formulated [10, 33, 71]. Nevertheless, several phenomenological investigations have correlated CGF processing variables such as particle hydrophobicity, frothing shear rate and time, and solids loading to bubble size and bubble content [10, 71]. To date, no structure-elasticity studies have been carried out, but preliminary observations show that CGFs may possess the requisite rheology for filamentary 3D printing [10, 50]. Therefore, linking CGF microstructure to elasticity would not only provide insight into the underlying physics of this unique class of soft materials, but it may also highlight guidelines for creating novel inks for AM of hierarchical cellular materials.
CHAPTER 3

MICROSTRUCTURE AND ELASTIC PROPERTIES OF COLLOIDAL GEL FOAMS

This chapter has been adapted from a manuscript in preparation for *Langmuir*:


3.1 INTRODUCTION

Foams and emulsions are widely used in pharmaceuticals [119], food [115, 123], cosmetics [124], and, most recently, as inks for 3D printing of lightweight architectures [33, 50]. Their stability, structure, and rheological properties must be tailored for each targeted application of interest. Due to the large excess area associated with the liquid-gas (foam) or oil-water (emulsion) interfaces, such systems are inherently unstable and cream, coalesce, or disproportionate in the absence of sufficient interfacial stabilization. Colloidal particles, which irreversibly adsorb onto these interfaces, are known to impart long term stability to both foams and emulsions, the latter of which are referred to as Pickering emulsions [74–78, 125, 126]. Particle stabilization is highly effective at preventing van der Waals collapse, retarding Ostwald ripening, and in some cases, arresting gravitational syneresis [74, 76, 77, 118, 126].

Interfacial stabilization arises when particles form an armor-like layer at the liquid-gas or oil-water interfaces [82, 83]. If all particles in the system adsorb onto the interfaces, interfacial stabilization is possible for colloid volume fraction ($\phi_c$) as low as ~ 0.0001-0.01, depending on the characteristic particle size and total interfacial area [119]. In this case, van der Waals collapse and Ostwald ripening are hindered by the interfacial particle layer [76, 77]. For repulsive interparticle interactions, the microstructure and elasticity of these systems are qualitatively similar to surfactant stabilized foams and emulsions [82, 83]. Namely, they possess negligible
elasticity below random close packing of the dispersed phase ($\phi_{rcp} = 0.635$) and gel-like elasticity above $\phi_{rcp}$ [110, 111]. For the particle-free case, several scaling laws have been proposed. Derjaguin [112], and later Wilson [113], showed that $G' \sim \sigma \Sigma$, where $\sigma$ is the surface tension and $\Sigma$ is the specific interfacial area (interfacial area per unit volume), in the limit where the volume fraction of the dispersed phase ($\phi_b$) approaches unity (so called “dry” systems). In their analyses, the polyhedral faces of the compressed foam cells store an amount of energy proportional to their surface tension and the amount of interfacial area in the system. Princen and Kiss [111], and more recently Mason and Weitz [110], described dispersed system elasticity over a broader $\phi_b$ range. Mason and Weitz showed $G' \sim \phi_b (\phi_b - \phi_{rcp}) \frac{\sigma}{r}$ where $r$ is the droplet radius. Their result emphasizes that elasticity in repulsive dispersed systems scales with the Laplace pressure, and arises when the system is compressed above close packing, allowing adjoining interfaces to transmit stress throughout the system. While particle stabilized systems exhibit similar scaling to their particle-free counterparts, their elasticity scales with the elasticity of the interfacial stabilizing layer instead of the Laplace pressure [82, 83, 124]. Interfacial stabilization can also occur when there are excess repulsive particles dispersed in the continuous phase, beyond what is necessary for forming particle-adsorbed interfacial layers [119, 127]. In this case, system stability is further enhanced due to the increased viscosity of the continuous phase, which retards fluid flow.

When attractive interactions are introduced between colloidal particles, the elasticity of the adsorbed particle layers increases [83, 128]. In some cases, individual particles may bridge two interfaces, forming a Pickering emulsion gel [114]. However, as the attractive particle volume fraction increases beyond that required solely for interfacial stabilization, excess particles within the continuous phase may form a space-filling particle network, ie., a colloidal
gel, provided $\phi_c > \phi_{gel}$ [116, 117, 120–122]. The addition of a dispersed phase (e.g., air or an immiscible liquid) to the continuous colloidal gel phase increases the elasticity of the system, where the bulk elasticity is now affected by the attractive particle network that surrounds bubbles or liquid drops within the dispersed phase. The elastic properties of these systems may be akin to attractive colloidal systems [102–104, 106], i.e., $G' \sim \phi^n_c$, where $G'$ depends on the volume fraction of the particles in the continuous phase [83, 114, 129]. The presence of this attractive particle network can provide additional stability to these foams [115, 117–119, 121].

To date, most studies have focused on particle-stabilized systems in which the droplet/bubble volume fraction and stability are maximized, while retaining excellent flow properties [77, 78, 83]. These design criteria favor systems with repulsive or weakly attractive interparticle interactions and low $\phi_c$ [78]. However, recent efforts to develop particle-stabilized foams and emulsions for 3D printing of hierarchical porous materials underscores the need for far higher solids loadings as well as strong attractive interactions between particles in the continuous phase to facilitate fabrication [33, 50]. For example, we recently produced architected porous ceramics in the form of open honeycomb lattices composed of printed closed cell foam struts via direct foam writing (see Chapter 4) [33]. Upon sintering, these hierarchical structures exhibited excellent mechanical properties, including high specific stiffness. However, fundamental understanding of these concentrated attractive particle-based systems, which we refer to as colloidal gel foams, is currently lacking.

In this chapter, we investigate the stability, microstructure, and elasticity of colloidal gel foams (CGFs) created by mechanically frothing aqueous suspensions of attractive alumina particles of varying composition. Prior to foaming, the pure colloidal gels exhibit a solid-like response, with a frequency independent shear elastic modulus ($G'$) that exceeds the shear loss
modulus ($G''$) in the linear viscoelastic regime, fluid-like characteristics ($G' < G''$) at stresses ($\tau$) exceeding a critical yield stress ($\tau_y$), a strong power law dependence of $G'$ on $\phi_c$, and plateau modulus ($G'_c$) that is roughly two orders of magnitude lower than their foamed counterparts ($G'_f$) (Figure 3.1-3.2). By controlling the foaming intensity, particle hydrophobicity and interparticle interactions via surfactant concentration, chain length, pH, and colloid volume fraction of the precursor gels, we produce stable CGFs with distinct microstructural and elastic characteristics. These foams exhibit similar rheological characteristics to their precursors, i.e., pure colloidal gels [95, 102–104, 106]. We determine the processing window for producing stable CGFs and show that foam elasticity scales nearly linearly with the specific interfacial area between the continuous (gel) and dispersed (bubble) phases, rather than $\phi_c$ as expected for pure colloidal gels in the absence of dispersed bubbles [102–104, 106]. Our results provide new insights into the structure-elasticity relationships of colloidal gel foams as well as processing guidelines for creating novel inks for additive manufacturing of hierarchically porous materials.
Figure 3.1: Microstructure and elasticity of colloidal gel foams (CGFs). (A) Scheme of CGF structure in which particle stabilized bubbles are connected by the gel network of the continuous phase. Bubble stabilization is enabled by controlling the contact angle of the particles such that they spontaneously adsorb on the liquid-gas interface. Images of a representative CGF wet microstructure (B) immediately after foaming and (C) one week after foaming (Scale bars: 500 μm). Bubble volume fraction ($\phi_b$) and bubble size ($d$) are nearly identical between each image, indicating effective stabilization. Plots of (D) apparent viscosity as a function of shear rate, storage ($G'$) and loss moduli ($G''$) (E) as function of frequency ($\omega$) and (F) shear stress ($\tau$), for the representative precursor gel and its corresponding CGF. Reported storage moduli values are taken at $\omega = 10$ rad/s.
Figure 3.2: Shear elastic modulus ($G'$) for precursor gels with variable solids loading and hydrophobization equivalent to the reference formulation. (A) $G'$ as a function of frequency ($\omega$). All moduli values correspond to $G'$ at $\omega = 10$ rad/s. (B) $G'$ as a function of solids loading ($\phi_c$). The slope of the power law fit is similar to other attractive colloidal systems with high solids loading [95, 107].

3.2 EXPERIMENTAL

3.2.1 Materials System

Colloidal gels and CGFs are produced by first suspending an appropriate amount of $\alpha$–alumina particles (AKP 30; Sumitomo Chemical; mean diameter = 300 nm and Brunauer-Emmett-Teller surface area ~ 7.5 m$^2$/g) in deionized (DI) water at pH< 3 (adjusted by adding hydrochloric acid, HCl) to produce a well dispersed colloidal suspension ($\phi_c = 0.51$). This stock suspension is mixed in a planetary mixer (SpeedMixer DAC 600.2; FlackTek, Inc.) for 1 minute at 800, 1200, and 1600 rpm, and 7 minutes at 2000 rpm to disperse the alumina particles, followed by ball milling for at least 48 h using 5 mm yttria-stabilized zirconia spherical milling media in a 2:1 mass ratio relative to the suspension. After milling, $\Lambda$, the desired amount of sodium-X-sulfonate, where the number of alkane carbons ($X$) varies from 5 to 7 (i.e., sodium-pentanesulfonate ($X = 5$), Sigma Aldrich; sodium-hexanesulfonate ($X = 6$), Sigma Aldrich;
sodium-heptanesulfonate \((X = 7)\), Alfa Aesar, respectively) is added per m² of colloid surface area to partially hydrophobize the alumina particles [130]. Colloidal gels are produced from this stock suspension by adjusting their final \(\phi_c\) (0.25-0.45) and pH through the addition of DI water and either sodium hydroxide or nitric acid. After each addition, the suspension is mixed for 2 minutes at 2000 rpm. Once the desired solids loading and pH have been achieved, the resulting colloidal gel is characterized within 24 h.

To create the desired CGFs, 60 g of each representative colloidal gel is foamed in a 240 mL glass jar (SS CLR; VWR). Air is entrained using a four bladed impeller (316L Cross Stirrer; Scilogex) and overhead mixer (OS20-S; Scilogex) at 400, 500, 750, 900, 1100, 1200, and 1500 rpm for 5 minutes each. Final foaming is performed with a flat-bottomed whisk (Triangular 10.5” Flat Bottom Whisk; Rattleware) at 1500 rpm for 1.5 min in the presence of an air stream. Foaming intensity levels are denoted by: 25% (400 rpm), 50% (750 rpm), 75% (1100 rpm), 100% (1500 rpm), 100W% (100% + whisk), where a given intensity level includes all lower intensities. All foams are characterized immediately after foaming unless otherwise stated. CGFs are defined as unstable, when any coarsening or drainage occurs within the first 24 h period. By contrast, the total bubble content and mean bubble size are retained in stable CGFs for at least 1 week (Figure 3.1).

### 3.2.2 Microscopy and Image Analysis

The bubble volume fraction \((\phi_b)\) and diameter \((d)\) are obtained for each foam by carrying out image analysis on micrographs acquired by transmission optical microscopy (VHX 2000, Keyence). Images are taken immediately after producing CGFs of varying composition. \(\phi_b\) is obtained using the systematic point count method (ASTM E562-08). At least 420 grid points are analyzed over 12.2 mm² for each wet foam. \(d\) is obtained using the linear intercept method for
two-phase materials (ASTM E112-13), where bubbles are defined as the dispersed phase and the alumina gel is defined as the continuous phase. At least 60 mm of lines are analyzed over 12.2 mm². To ensure equal interfacial area comparison between CGFs with different bubble content, interfacial area is reported per unit volume of foam and is calculated from \( \phi_b \) and \( d \) according to \( \Sigma=\frac{\left(6\phi_b\right)}{d}\times1000 \) where \( d \) is in \( \mu \)m, 1000 is a unit conversion from \( \mu \)m to mm, and \( \Sigma \) has units of mm²/mm³ or mm⁻¹ [131]. Reported averages and standard deviations correspond to values obtained from at least three different images.

3.2.3 Contact Angle Measurements

Static contact angle measurements are performed by depositing 20 \( \mu \)L drops of diluted precursor suspensions at an infill rate of 60 \( \mu \)L/min onto the surface of a polished and cleaned sintered \( \alpha \)-alumina (AKP 30; Sumitomo Chemical) plate. The droplet suspensions are made according the process outlined for the precursor gels in 3.2.1. However, after formulation they are diluted in a 1:5 volumetric ratio with water and the appropriate pH modifier to maintain constant pH. Measurements are taken after allowing the droplet to equilibrate for five seconds. All reported values represent the average and standard deviation obtained from at least five separate measurements.

3.2.4 Rheometry

The rheological properties of the precursor colloidal gels and CGFs are characterized at 21°C using a controlled stress rheometer (Discovery HR-3 Hybrid Rheometer; TA Instruments). A 40 mm tapered cone geometry (2.005°, 56 \( \mu \)m truncation gap) is used for the gels, while a custom made 8-bladed vane (15 mm diameter, 38.5 mm height, 1.3 mm blade thickness, 4 mm gap) is used for the CGFs. A solvent trap is used for all tests to prevent solvent loss. Prior to testing, all gels are homogenized for 1 min at 2000 rpm, then carefully placed on the rheometer.
stage using a spatula. CGFs are tested immediately after frothing and loaded into the cup using a custom dispensing system to minimize differences in loading conditions between specimens. Prior to acquiring measurements, each sample is allowed to equilibrate for at least 15 min while undergoing low amplitude oscillatory strain ($\gamma$) ($\gamma = 0.001\%$, which is within the linear viscoelastic regime (Figure 3.3) or until $G'$ varied negligibly over the experimental time scale. After equilibration, frequency sweeps are performed between $0.1 - 100$ rad/s with strain amplitude of $0.001\%$. $G'$ of the CGF and precursor gel ($G'_c$) are taken at $\omega = 10$ rad/s. Error bars correspond to $G'$ at 1 rad/s (lower bound) and 100 rad/s (upper bound). Oscillatory sweeps are performed from $0.00006 - 100\%$ strain at 1 Hz. The shear yield stress, $\tau_y$, is defined by the crossover point where $G''$ exceeds $G'$. Flow sweeps are carried out between 0.001-250 s$^{-1}$.

![Figure 3.3: Storage ($G'$) and loss ($G''$) moduli as a function of shear strain ($\gamma$) for the (A) least stiff, and (B) stiffest gels, and their corresponding CGFs explored in Figure 3.6. $\gamma = 1\times10^{-3}\%$ is well within the linear viscoelastic regime for all formulations.](image)

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3.3 RESULTS AND DISCUSSION

3.3.1 CGF Production

CGFs of varying composition are produced by mechanically frothing aqueous suspensions of partially hydrophobized alumina particles. When the interfacial tensions of the solid-liquid ($\sigma_{sl}$), liquid-gas ($\sigma_{lg}$), and solid-gas interfaces ($\sigma_{sg}$) are balanced such that the contact angle ($\theta$) of the particles and the solvent lies between the calculated range of 14° and 90° for a mean particle diameter of 300 nm, the particles irreversibly and spontaneously adsorb onto liquid-gas (bubble) interfaces introduced during foaming (Figure 3.1A) [74, 76, 77, 91, 125, 126]. The adsorbed particles physically prevent the dispersed bubble phase from van der Waals collapse and Ostwald ripening, and for sufficiently attractive interparticle interactions, arrest drainage, yielding a stable foam microstructure that retains its characteristic bubble content and size over long times [14]. Direct imaging of wet foams stabilized by alumina particles (partially hydrophobized with $\Lambda = 0.6 \, \mu$mol of $X = 6 \, /m^2$, and a measured contact angle with water of 62° ± 5°) immediately after production (0 days) and aging (7 days) demonstrate that their $\phi_b$ (60.0 ± 3% and 59.0 ± 5%, respectively) and $d$ (34.9 ± 2.7 μm and 33.9 ± 3.2 μm, respectively) remain nearly constant (Figure 3.1B-C).

The rheological properties of a representative precursor colloidal gel and CGF ($\Lambda = 0.6 \, \mu$mol of $X = 6 \, /m^2$, pH=5, $\phi_c = 0.35$) are shown in Figure 3.1D-F. Under these conditions, the colloidal particles are attractive, resulting in the formation of a colloidal gel that exhibits strong shear thinning behavior with an apparent viscosity ranging from ~1000 Pa·s at $10^{-3}$ s$^{-1}$ to ~0.06 Pa·s at $10^{2}$ s$^{-1}$. During mechanical foaming, the colloidal gel network is subjected to high shear rates that disrupt the attractive interparticle bonds thereby allowing individual particles to adsorb onto the liquid-air interface during air entrainment. However, once foaming ceases, the attractive
particle network quickly reforms under quiescent conditions and surrounds each entrained air bubble. The plateau $G' (~2 \cdot 10^3 \text{ Pa})$ and $\tau_y (~30 \text{ Pa})$ of the colloidal gel network is sufficiently high to prevent syneresis, which occurs in colloidal fluids frothed at pH < 4.5. Notably, after foaming the CGFs exhibit a sharp rise in their apparent viscosity, which increases by more than an order of magnitude over all shear rates investigated, along with a concomitant increase in the plateau $G' (~10^5 \text{ Pa})$ and $\tau_y (~10^2 \text{ Pa})$.

3.3.2 Foaming Intensity Effects on CGF Structure and Elasticity

Next, we investigate the effects of mechanical foaming intensity on the microstructural and rheological property evolution of this representative CGF ($\Lambda = 0.6 \mu\text{mol of } X = 6 \text{ /m}^2, \text{pH} = 5, \phi_c = 0.35$) (Figure 3.4). As foaming intensity increases from 25% to 100W% (see 3.2.1 for foaming process details), $\phi_b$ increases from 0.20 to 0.60, while $d$ decreases from 158 $\mu\text{m}$ to 35 $\mu\text{m}$ (Figure 3.4F). The foaming process leads to a concomitant increase in $\Sigma$ from 7.5 mm$^2$/mm$^3$ to 103 mm$^2$/mm$^3$ over the same intensity range (Figure 3.4G). Increasing foaming intensity also produces stiffer CGFs. $G'_f$ increases by over an order of magnitude over the full foaming intensity range (6.7x10$^3$ Pa at 25% to 1.3x10$^5$ Pa at 100W%) (Figure 3.4H).
**Figure 3.4: Foaming intensity effect on CGF microstructure and elasticity.** (A-E) Images of the CGF microstructure at 25%, 50%, 75%, 100%, and 100W% foaming intensity, respectively (Scale bars: 500 μm). (F) Plots of bubble volume fraction ($\phi_b$), bubble size ($d$), and (G) specific interfacial area ($\Sigma$) as a function of foaming intensity. Plots of storage modulus ($G'$) as function of (H) frequency ($\omega$), and (I) $\phi_{\text{int}} / \phi_c$, at the foaming intensities represented in (A-E).

We hypothesize that the increased elastic response of CGFs relative to their precursor gels may be related to the fraction of particles adsorbed on bubble interfaces ($\phi_{\text{int}}$). To estimate $\phi_{\text{int}}$, we approximate each CGF structure as a monodisperse system of spherical bubbles with size $d$, where the midplane of each adsorbed colloidal particle resides on the bubble interface. Because the particle stabilization process is a spontaneous surface phenomenon, the packing of adsorbed colloids on the bubble interfaces is two dimensional and should range between the van der Waerden [132, 133] lower bound for small particles packing on large spheres (Equation 3.1, where $P_{\text{vdw}}$ is the packing fraction of particles on the interface, $r_p$ is the particle radius, and $N_{\text{vdw}}$ is number of interfacial particles that can adsorb on a single bubble (Equation 3.2)) and hexagonal packing (0.906) [134].
\[ P_{vdw} = \frac{N_{vdw} r_p^2}{4(r_p+\frac{d}{2})^2} \]  
(3.1)

\[ \left( \frac{r_p + \frac{d}{2}}{r_p} \right)^2 = 2\sqrt{3} \left( \frac{N_{vdw}}{4\pi} \right) + 3 \left( \frac{N_{vdw}}{4\pi} \right)^\frac{2}{3} + 3 \left( \frac{N_{vdw}}{4\pi} \right)^\frac{1}{3} \]  
(3.2)

(Note, perfect hexagonal packing is not rigorously feasible in curved systems due to disclinations that form to accommodate bubble curvature. Nonetheless, it serves as a useful limit for systems where \( r_p << d/2 \) [133, 135, 136].) For a given CGF, it is straightforward to determine the volume of the continuous phase from \( \phi_b \), allowing \( \phi_{int} \) to be calculated according to \( \phi_{int} = \frac{(N_i V_p)}{V_c} \), where \( N_i \) is the total number of interfacial particles, \( V_p \) is the volume of an individual colloidal particle, and \( V_c \) is the total volume of the continuous phase. Figure 3.4I shows the evolution of \( G' \) with the normalized volume fraction of interfacial particles in the van der Waerden limit. At the lowest foaming intensity level, less than \( \sim 0.5\% \) of the particles within the CGF are adsorbed on the bubble interfaces, yet \( G'_f \) is four-fold higher than that of the pure colloidal gel, \( G'_c \). At the maximum foaming intensity, \( \phi_{int}/\phi_c = 0.12 \) and \( G'_f \) is nearly two orders of magnitude higher than \( G'_c \). This dramatic increase in CGF stiffness may arise from the significant adsorption energies (\( \sim 10^3 kT \) or higher for 300 nm particles) associated with each particle adsorbed at the liquid-air interface [14, 76]. This pinning energy is far higher than the estimated attractive interparticle bonds (\( \sim \) few to 10 \( kT \)) between particles in the gel network [106]. Moreover, because the interfacial particles are more densely packed relative to the continuous gel phase [72], they give rise to highly elastic, armor-like, layers that dramatically affect bulk elasticity [82, 83, 124]. The observed increases in \( G'_f \) with increasing \( \Sigma \) (and therefore \( \phi_{int} \)) occur well below \( \phi_{rcp} \), since the continuous gel network within the CGF binds the interspersed bubbles together, effectively transmitting stress to the bubble interfaces through the backbone of interconnected particle
clusters within the gel (Figure 3.1A). Similar trends are observed for all CGFs studied (Figure 3.5).

![Figure 3.5: Storage modulus (G') as a function of the volume fraction of particles adsorbed on bubble interfaces (φ_{int}) normalized by the total solid volume fraction (φ_c) for a variety of precursor gel formulations (A) in the van der Waerden (B) hexagonal limits for particle packing. In all cases, G' increases with increasing with φ_{int}/φ_c.](image)

3.3.3 Effects of Precursor Colloidal Gel Composition on CGF Structure and Elasticity

CGF structure and elasticity can also be manipulated through the composition of the colloidal (precursor) gel by altering Λ, X, pH, or φ_c. The effects of each of these variables on CGF structure and elasticity are explored in Figure 3.6-3.8 and Table 3.1 in which each CGF is subjected to maximum (100W%) foaming. Particle hydrophobicity is modified by varying the sodium hexanesulphonate concentration from 0.3 – 0.9 µmol/m² and alkane length from X = 5 – 7 at Λ = 0.6 µmol/m² (Figure 3.6A-B). We find that the contact angle for all Λ and X studied lies within the range of 48° – 64° with no systematic dependence on surfactant concentration or length [137]. Importantly, G'_c and G'_f are nearly constant over the entire range of surfactant
concentrations and alkane lengths investigated, i.e., $G'_c$ ranges from $1.2 \times 10^3$ to $2.0 \times 10^3$ Pa for pure colloidal gels, while $G'_f$ ranges from $6.3 \times 10^3$ Pa to $1.9 \times 10^4$ Pa for the CGFs.

Figure 3.6: Storage modulus ($G'$) and specific interfacial area ($\Sigma$) as a function of (A) surfactant concentration, (B) surfactant length, (C) pH, and (D) solids loading ($\phi_c$). Solid and hatched bars represent CGF and gel characteristics, respectively.
Figure 3.7: Alkane length (X) and colloid volume fraction (φc) effects on CGF microstructure. (A-C) Images of CGFs with X = 5, 6, 7, respectively, and otherwise constant conditions (Scale bars: 500 μm). (D) Plot of bubble volume fraction (φb) and bubble size (d) as function of surfactant chain length. (E-G) Images of CGFs with φc = 0.25, 0.35, 0.45, respectively, and otherwise constant conditions (Scale bars: 500 μm). (H) Plot of bubble volume fraction (φb) and bubble size (d) as function of φc.
Figure 3.8: Microstructures of CGFs with various surfactant concentrations ($\Lambda$) and suspension pH. (A-C) Images of CGFs with $\Lambda = 0.3$, 0.6, 0.9 $\mu$mol/m$^2$, respectively, and otherwise constant conditions (Scale bars: 500 $\mu$m). (D) Plot of bubble volume fraction ($\phi_b$) and bubble size ($d$) as function of $\Lambda$. (E-G) Images of CGFs with pH = 4.5, 5.0, 5.5, respectively, and otherwise constant conditions (Scale bars: 500 $\mu$m). (H) Plot of bubble volume fraction ($\phi_b$) and bubble size ($d$) as function of pH.

Table 3.1: Formulation, microstructure, and elasticity information for colloidal gels and CGFs in Figure 3.6.

<table>
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<th>$\phi_c$</th>
<th>$\phi_b$</th>
<th>d (µm)</th>
<th>$\Sigma$ (mm$^{-1}$)</th>
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<td>15±2.1</td>
<td>152±8.8</td>
<td>1.2x10$^3$</td>
<td>2.9x10$^5$</td>
</tr>
</tbody>
</table>
While particle hydrophobicity minimally affects the elasticity of the colloid gel precursors and CGFs over the experimental conditions explored, increasing particle hydrophobicity via longer alkane chain length significantly impacts CGF microstructure. The micrographs in Figure 3.7 show that as surfactant length increases from $X = 5$ to $X = 7$, $\phi_b$ increases from 0.33 to 0.57 and $d$ decreases from 69 $\mu$m to 27 $\mu$m. Together, these changes significantly increase $\Sigma$ from 29 mm$^2$/mm$^3$ to 126 mm$^2$/mm$^3$ for $X = 5$ and $X = 7$, respectively. The effects of $\Lambda$ on CGF structure are minimal compared to the alkane chain length. $\phi_b$, $d$, and $\Sigma$ range from 0.32 to 0.47, 61 $\mu$m to 51 $\mu$m, and 33 to 55 mm$^2$/mm$^3$, respectively, for $\Lambda$ values between 0.3 $\mu$mol/m$^2$ and 0.9 $\mu$mol/m$^2$ (Figure 3.8).

Interparticle bond stiffness, reflected by $G'_c$, also affects CGF properties, and can be modulated by pH. As pH is varied from 4.5 to 5.5 (i.e., closer to the isoelectric point (IEP) of alumina, (pH ~9)), the electrostatic repulsion between particles is reduced, leading to a modest increase in $G'_c$ from $1.02 \times 10^2$ to $4.0 \times 10^3$ Pa. Over the same pH range, $\phi_b$ increases from 0.36 to 0.49, $d$ decreases from 66 $\mu$m to 49 $\mu$m, and $\Sigma$ increases from 33 mm$^2$/mm$^3$ to 60 mm$^2$/mm$^3$, respectively. We attribute the increase in $\Sigma$ to changes in suspension stiffness, rather than changes in particle hydrophobicity, because less surfactant likely adsorbs onto the particles at higher pH values due to their lower positive charge. Higher pH values also correspond to stiffer CGFs. $G'_f$ increases by an order of magnitude from $2.9 \times 10^3$ Pa at pH 4.5 to $2.8 \times 10^4$ Pa at pH 5.5. Higher pH fosters stronger interparticle attraction and increased flocculation in the continuous phase, while increased $\Sigma$ promotes higher $\phi_{int}$ and additional interbubble bond formation. Both factors enhance the elasticity of these CGF systems [109, 116, 117, 119].

The number density of attractive interparticle bonds scales with $\phi_c$ [138]. As $\phi_c$ increases from 0.25 to 0.45, $G'_c$ increases dramatically from $7.6 \times 10^1$ Pa to $1.2 \times 10^4$ Pa, respectively (Figure
Interestingly, we find that systems with \( \phi_c \) equal to 0.25 have nearly the same \( \Sigma \) and higher \( G'_f \) as systems with \( \phi_c \) equal to 0.35, even though \( G'_c \) is 10x higher in the latter case. As Figure 3.7 illustrates, their similarity in \( \Sigma \), values of 52 and 50 \( \text{mm}^2/\text{mm}^3 \), respectively, arises due to differences in bubble morphology. CGFs prepared from precursor gels composed of \( \phi_c = 0.25 \) possess higher bubble content (\( \phi_b = 0.68 \)) and larger bubble size (\( d = 79 \mu\text{m} \)). By contrast, CGFs prepared from precursor gels with \( \phi_c = 0.35 \) possess fewer, but smaller bubbles (\( \phi_b = 0.45, d = 54 \mu\text{m} \)). Moreover, these morphology differences suggest that the increased stiffness of CGFs with \( \phi_c \) equal to 0.25 compared to CGFs with \( \phi_c \) equal to 0.35 may stem from bubble interface distortion since \( \phi_b > \phi_{\text{rep}} \) [83]. The stiffest CGF arises from the most concentrated precursor gel, \( \phi_c = 0.45 \), explored. Due to its high \( G'_c \), smaller bubbles (\( d = 14 \mu\text{m} \)) are incorporated, leading to the highest \( \Sigma \) and \( G'_f \) values of 152 \( \text{mm}^2/\text{mm}^3 \) and 2.9 \( \times 10^5 \) Pa, respectively, despite having \( \phi_b < 0.40 \).

The total effects of increasing particle hydrophobicity, interparticle bond stiffness and interparticle bond density on \( G'_c, \Sigma, \) and \( G'_f \) suggest that interfacial stabilization contributes predominantly to the microstructural evolution of these colloidal gel foams, but only modestly influences their elasticity. This is best illustrated by the nearly four-fold increase in \( \Sigma \) that is accompanied by only a three-fold increase in \( G'_f \) as \( X \) increases from \( X = 5 \) to \( X = 7 \). By contrast, the particle network strongly affects the foam morphology and stiffness. Both pH (bond stiffness) and \( \phi_c \) (bond density) increases lead to a pronounced increase in \( \Sigma \). Moreover, the elasticity of CGFs increases over an order of magnitude over these experimental conditions. Our observations indicate that particle hydrophobicity can be used to tailor foam microstructure without dramatically affecting elasticity while changes in pH and \( \phi_c \) effectively alter both properties.
3.3.4 CGF Stability

While the microstructure and elasticity of CGFs are of primary interest, we also explored the stability of CGFs to understand the range of achievable properties. A stability map for CGFs prepared with $\phi_c = 0.35$, varying particle hydrophobicity and foaming intensity is shown in Figure 3.9A. Stable foams are obtained between pH 4.5 and 6.75 with $\Sigma$ values ranging from 3.3 – 233 mm$^2$/mm$^3$ (Table 3.2). In this pH range, the precursor gel is sufficiently stiff to entrap bubbles, but not excessively stiff so as to preclude foaming. In principle, stable foams are accessible up to pH values approaching the IEP with sufficiently energetic aeration. However, the energy required to create new interfacial area ($E_{\text{int}}$) in precursor gels with pH > 6.75 exceeded that provided by our experimental equipment ($E_{\text{mix}}$). Within the stable region, the maximum $\Sigma$ value at each pH starts at 152 mm$^2$/mm$^3$ at pH = 4.5, peaks at 233 mm$^2$/mm$^3$ at pH 5.5, and then decreases again to 136 mm$^2$/mm$^3$ at pH 6.75. Between pH 5.5-6.75, the stiffness of the precursor gel increases from $4.6 \times 10^4$ Pa to $1.8 \times 10^5$ Pa. We hypothesize that comparatively higher input energy is required to break apart particulate clusters within stiffer gels in order to accommodate additional interfacial area.[119] As interfacial area is introduced, more particles adsorb on interfaces and more bonds between bubbles form, increasing the CGF stiffness until $E_{\text{mix}} < E_{\text{int}}$, after which aeration ceases. Between pH 4.5 - 5.5, $G_c$ increases from $7.6 \times 10^1$ Pa to $4.6 \times 10^4$ Pa. Over this pH range, stiffer gels are capable of entraining smaller bubbles without compromising $\phi_b$, leading to higher $\Sigma$. Note, $\phi_b$ is similar between pH 4.5 ($\phi_b = 0.56$) and pH 5.5 ($\phi_b = 0.53$), but foams prepared at pH 5.5 possess bubbles that are 40% smaller in size than those found at pH 4.5, i.e., $d = 14$ µm and $d = 22$ µm, respectively. However, as the gel becomes increasingly stiff, a significant reduction in $\phi_b$ occurs (pH 6.75: $\phi_b = 0.37$), yielding lower $\Sigma$. Therefore, the maximum realizable $\Sigma$ between pH 4.5 - 5.5 is limited by gel stiffness, whereas between pH 5.5 -
6.75, it is limited by \( E_{\text{mix}} \). While bubbles could be entrained in the precursor suspensions below pH 4.5, these foams are unstable and cream within 24 h.
Figure 3.9: Stability and elastic properties of CGFs. (A) Map of specific interfacial area ($\Sigma$) and pH for CGFs formulated with colloid volume fraction ($\phi_c$) = 0.35 and surfactant concentration ($\Lambda$) = 0.6 µmol/m$^2$ highlighting regions of stable and unstable CGFs. The hatched region would theoretically produce stable CGFs, but is experimentally inaccessible due to excessive gel stiffness. Plots of storage modulus ($G'$) vs $\Sigma$ for (B) the representative CGF formulation, and (C) CGFs at pH 4.5, 5.0, and 5.5 for various $\phi_c$ and alkane chain length ($X$).
Table 3.2: Stability, microstructure and elasticity details for data shown in Figure 3.9A.

<table>
<thead>
<tr>
<th>Stability Region</th>
<th>Point</th>
<th>pH</th>
<th>$\Sigma$ (mm$^2$)</th>
<th>$\phi_b$</th>
<th>d (μm)</th>
<th>$G'$ (Pa) 10 rad/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unstable</td>
<td>Upper pH boundary</td>
<td>4</td>
<td>137±11</td>
<td>0.52±0.04</td>
<td>23±3.6</td>
<td>3.3x10$^4$</td>
</tr>
<tr>
<td>Stable</td>
<td>Lower pH boundary</td>
<td>4.5</td>
<td>152±11</td>
<td>0.56±0.01</td>
<td>22±1.9</td>
<td>7.6x10$^4$</td>
</tr>
<tr>
<td></td>
<td>Maximum $\Sigma$</td>
<td>5.5</td>
<td>233±0.9</td>
<td>0.53±0.06</td>
<td>14±1.6</td>
<td>4.6x10$^4$</td>
</tr>
<tr>
<td></td>
<td>Minimum $\Sigma$</td>
<td>5.5</td>
<td>3.3±0.3</td>
<td>0.10±0.04</td>
<td>75±3.3</td>
<td>4.6x10$^4$</td>
</tr>
<tr>
<td></td>
<td>Upper pH boundary</td>
<td>6.75</td>
<td>137±15</td>
<td>0.37±0.02</td>
<td>16±2.2</td>
<td>1.8x10$^5$</td>
</tr>
</tbody>
</table>

Our results suggest the stiffness of the gel network critically impacts CGF stability. The presence of temporary, yet ultimately unstable, dispersed bubbles below pH 4.5 indicates that adequate particle hydrophobicity alone, and therefore interfacial stabilization, cannot stabilize the bulk foam if the continuous phase is not stiff enough to resist creaming. However, as the gel becomes stiff enough to resist creaming above pH 4.5, CGFs with bubble content ranging from nearly arbitrarily low $\Sigma$ to $\Sigma$ well above 150 mm$^2$/mm$^3$, are possible until $E_{mix} < E_{int}$. It is expected that for $\phi_c < 0.35$, the same stability trends would occur except the stability threshold pH would increase to compensate for lower interparticle bond density. Conversely, for $\phi_c > 0.35$, stability should begin at lower pH since bond density will be higher. Lastly, for insufficiently hydrophobic particles, it is well known that no foaming will occur regardless of network structure [78].

3.3.5 Behavior of CGF Elasticity

To evaluate the scaling of $G'$ with $\Sigma$, we create CGFs from nine different precursor formulations with $X = 6$ or 7 and $\phi_c = 0.25$ or 0.35 over three different pH values within the stable pH region. For each formulation, the surfactant concentration is fixed at 0.6 μmol/m$^2$, foaming intensity ranges between 25% to 100W%, and $\Sigma$ and $G'$ are measured at each foaming
level. Results for the reference CGF are shown in Figure 3.9B. As foaming intensity increases, $\Sigma$ and $G'_f$ increase from $7.5 \text{ mm}^2/\text{mm}^3$ and $6.7 \times 10^3 \text{ Pa}$ at 25% to $103 \text{ mm}^2/\text{mm}^3$ and $1.3 \times 10^5 \text{ Pa}$ at 100W%. Plotting $G'_f$ against $\Sigma$ shows this increase is linear with $\Sigma$, and the scaling exponent is near unity ($n = 1.09$, $r^2 = 0.96$). Remarkably, similar scaling is observed independent of $X$, $\phi_c$, or pH for all tested formulations ($n_{\text{avg}} = 1.12 \pm 0.18$) (Figure 3.10, Table 3.3). Furthermore, if $G'_f$ and $\Sigma$ are compared as a function of bond stiffness (i.e., pH), the same exponent value persists at each stiffness level (pH 4.5: $n = 1.17$, $r^2 = 0.81$, pH 5: $n = 1.13$, $r^2 = 0.92$ , pH 5.5: $n = 1.10$ , $r^2 = 0.92$), and the pre-exponential factor $c$, representing the effective interparticle bond stiffness in our proposed microstructure-elasticity model, increases with increasing pH from $2.56 \text{ Pa} \cdot \text{mm}^n$ at pH 4.5 to $3.02 \text{ Pa} \cdot \text{mm}^n$ at pH 5.5 (Figure 3.11).

Figure 3.10: Plots of storage modulus ($G'_f$) as a function of specific interfacial area ($\Sigma$) showing the scaling relationships for individual CGF formulations for the same CGFs in Figure 3.9 at (A) pH 4.5, (B) 5.0, and (C) 5.5.
Table 3.3: Data and fitting results for CGF formulations in Figure 3.9-3.10

<table>
<thead>
<tr>
<th>pH</th>
<th>(\phi_c)</th>
<th>X</th>
<th>Foaming Intensity (%):</th>
<th>(\Sigma) (mm(^3))</th>
<th>(G_f/10) rad/s</th>
<th>Formulation Fit</th>
<th>Global Fit</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>n</td>
<td>c (Pa·mm(^3))</td>
</tr>
<tr>
<td>4.5</td>
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<td>7</td>
<td></td>
<td></td>
<td></td>
<td>1.17</td>
<td>2.55</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.07</td>
<td>2.55</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td>1.31</td>
<td>2.55</td>
</tr>
<tr>
<td>5.0</td>
<td>0.35</td>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td>1.09</td>
<td>2.77</td>
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<td></td>
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<td></td>
<td>0.88</td>
<td>3.25</td>
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<td>0.86</td>
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</tr>
<tr>
<td></td>
<td>0.35</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td>1.08</td>
<td>3.10</td>
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<td></td>
<td>0.86</td>
<td>3.52</td>
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<td>0.86</td>
<td>3.52</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td>1.17</td>
<td>2.76</td>
</tr>
</tbody>
</table>

75
Figure 3.11: $c$ as a function of pH obtained from the regressions in Figure 3.9 and Table 3.3.

These observations may be explained by the proposed CGF structure shown in Figure 3.1A. We hypothesize that the partially hydrophobized particles adsorb on the bubble interfaces, while the continuous gel phase percolates between bubbles. The elasticity of the system arises from the interconnected bubble-filled gel network. For a given CGF, we assume that (1) interfacial characteristics are governed by the precursor formulation, (2) all interfaces within a given system have the same elastic properties, (3) there exists a fixed number of bonds per unit interfacial area, and (4) new interfacial area has the same probability of participating in interbubble bonding, as previously incorporated interfacial area [109]. By increasing $\Sigma$, at otherwise constant conditions, one should observe greater interbubble bonding along with a concomitant rise in $G'$. If our assumptions are correct, increasing $\Sigma$ via foaming intensity should produce a linearly proportional increase in interbubble bonds for a given foam formulation due to the increased connectivity of the bubble network. Importantly, this linearity should persist for all stable CGFs regardless of particle hydrophobicity and continuous phase structure. This finding is similar to the results reported by Derjaguin and Wilson for dry foams [112, 113], except we
hypothesize that the mechanism for stress transfer in their system (interfacial distortion), is replaced by attractive interparticle bridges that form between neighboring bubble interfaces.

The presence of attractive interparticle bonding influences the stiffness of the interbubble bonds as well as the stiffness of the armor-like particle stabilizing layer on the bubble interfaces. For CGFs with the same $\Sigma$, but different interparticle attraction, it is expected that the CGFs with stronger interparticle attraction will exhibit a larger $G'_f$. We observe this empirically when $c$ increases with increasing pH. Additional interfacial contributions to stiffness may arise when $\phi_b > \phi_{rcp}$, but for $\phi_b < \phi_{rcp}$ interbubble bonding is hypothesized to dominate the elastic response. Overall, we believe that the CGF microstructure consists of a network of particle stabilized bubbles connected by an attractive colloidal gel. The bulk elasticity of the bubble network depends linearly on the specific interfacial area, and stronger interparticle attractions give rise to more elastic foams.

3.4 CONCLUSIONS

In summary, we have explored the microstructure and elasticity of colloidal gel foams characterized by high solids loading and attractive interparticle interactions. By manipulating particle hydrophobicity, bond stiffness and density as well as foaming intensity, we created stable CGFs whose specific interfacial area and stiffness could be varied over two orders of magnitude. We also highlighted the boundary conditions for designing stable foams. Our observations suggest that CGF microstructures may be idealized as a network of particle stabilized bubbles connected by attractive particulate bridges that form within the continuous gel phase. Over all foam compositions studied, we find that the foam elasticity, $G'_f$, scales linearly with the specific interfacial area, $\Sigma$, associated with the gel-bubble interface. Finally, our
observations provide processing guidelines to further advance the directed assembly of porous architectures using colloidal gel foams.
CHAPTER 4

ARCHITECTED CELLULAR CERAMICS WITH

TAILORED STIFFNESS VIA DIRECT FOAM WRITING

This chapter has been adapted from the publication:


4.1 INTRODUCTION

Hierarchical cellular structures are ubiquitous in nature due to their mechanical efficiency and multifunctionality [5, 6, 36, 139]. Stochastic (foams) and periodic (two-dimensional honeycombs or three-dimensional lattices) cellular architectures exhibit either bending or stretching dominated mechanical responses depending on their nodal connectivity [30]. If structural motifs with different length scales are combined in a hierarchical manner within the same cellular structure, mixed-mode mechanical responses are possible [30], including stretching-stretching (e.g., wood along the grain [1]), bending-bending (e.g., cork across the grain [38]), and bending-stretching (e.g., bird wings [30], bones [6], wood across the grain [1]). Additional functionality is also enabled by natural cellular architectures, including buckling resistance (e.g., stems and quills [39]), thermal management (e.g., cork [38]), structural color (e.g., feathers [3, 4]) and fluid transport (e.g., bones and plants [3]).

Inspired by these natural systems, bulk and additive manufacturing methods have been developed to create synthetic analogs. For example, monolithic objects composed of open or closed-cell foams can be cast from particulate suspensions that contain pore-forming agents (i.e., porogens) [12] or particle stabilized foams (12, 13). While porous microstructures can be readily generated from myriad materials by those methods, they are limited to relatively simple
structures that possess bending-dominated mechanical responses [15, 140, 141]. Recently, multiscale metamaterials with properties heretofore unseen in engineered materials have been created by light-based 3D printing of photopolymerizable organic [16, 17, 26–28, 32] and preceramic resins [18]. Specifically, microlattices, octet structures, and tetrakaidecahedra with struts composed of hollow shells [17, 26, 27, 32], solid features [18, 28], or even finer trusses [16, 17] have been produced, which may exhibit bending, stretching, or mixed mode mechanical responses. However, these lattices are limited to open architectures constructed using photopolymerizable materials that must be subsequently transformed to ceramic or metal through some combination of coating and pyrolysis. Recent advances in directly printing ceramic [19] and metal [21] lattices open new avenues for lightweight structural components [5], thermal insulation [53], tissue scaffolds [8], catalyst supports [7], and electrodes [9].

In this chapter, we report the fabrication and characterization of architected cellular ceramics with tunable microstructure, geometry, and stiffness via direct foam writing. Specifically, we print filamentary struts containing a closed-cell foam microstructure periodically arrayed in the form of hexagonal or triangular honeycombs (Figure 4.1). Our colloidal gel foam (CGF) ink contains significant porosity that arises from entrained bubbles surrounded by colloidal particles in an aqueous suspension. By carefully controlling ink composition, print path, drying and sintering conditions, we can programmably create architected cellular ceramics composed of bending, stretching, bending-bending, or stretching-bending dominated unit cells, whose density and stiffness can be tailored over at least one order of magnitude. Importantly, these hybrid (open-closed cell) architectures exhibit exceptional specific stiffness compared to structures produced by either bulk foam casting or light-based 3D printing.
4.2 EXPERIMENTAL

4.2.1 Colloidal Gel Foam Ink

The foam ink is created by first producing an aqueous colloidal suspension composed of 45 vol% α-alumina (mean particle size ~ 300 nm, BET surface area ~ 7.5 m²/g) (AKP 30; Sumitomo Chemical) and deionized (DI) water at pH< 3 (the pH is adjusted by adding hydrochloric acid, HCl). The suspension is mixed in a planetary mixer (SpeedMixer DAC 600.2; FlackTek, Inc.) for 1 minute at 800, 1200, and 1600 rpm, and 7 minutes at 2000 rpm to disperse the alumina, and ball milled for at least 48 h using 5 mm yttria-stabilized zirconia spherical milling media in a 2:1 mass ratio relative to the suspension. After ball milling, 4.8 µmol of butyric acid (Sigma Aldrich) is added per m² of colloid surface area to partially hydrophobize the
alumina particles. (Note this surfactant differs from those investigated in Chapter 3, but it is equally effective at producing the desired foam inks.) The suspension is then weakly gelled by adding sodium hydroxide (NaOH) until the pH is increased to 5-5.1. DI water, polyethylene glycol (1 wt% relative to alumina), (20,000 g/mol; Sigma Aldrich), and rice starch (2 wt% relative to water) (HRICE 16; Hollander’s) are added to the gel prior to frothing to dilute the suspension to 35 vol% solids, strengthen printed structures, and retard drying, respectively. After each addition, the suspension is mixed for 2 minutes at 2000 rpm. All frothing is performed in a 500 mL glass jar (SS CLR; VWR) using 75 g of the precursor gel. Air is introduced via a four bladed impeller (316L Cross Stirrer; Scilogex) and overhead mixer (OS20-S; Scilogex) at 400, 500, 700, 900 rpm for 2 minutes each and then at 1000, 1200, and 1500 rpm for 5 minutes each. Final frothing is performed with a flat-bottomed whisk (Triangular 10.5” Flat Bottom Whisk; Rattleware) at 1200 rpm for 2 min in the presence of an air stream.

4.2.2 Pure Colloidal Ink

To print nearly dense honeycombs, we created a pure (bubble-free) colloidal ink composed of 55 vol% α-alumina particles (AKP 30; Sumitomo Chemical) suspended in DI water and stabilized using 1 mg of an anionic polyelectrolye dispersant (Darvan 821a; R. T. Vanderbilt Company) per m² of alumina surface area. The suspension is mixed at 1700 rpm for 10 min to disperse the alumina particles. The solution is then ball milled for at least 48 h using 5 mm yttria-stabilized zirconia spherical milling media in a 2:1 mass ratio relative to the suspension. After milling, 7 mg of hydroxypropyl methylcellulose (Methocel F4M; Dow Chemical Company) is added per mL of alumina in the form of a 5 wt% aqueous solution. The pH is adjusted to 7 using NaOH or nitric acid as necessary, and the suspension is diluted to 51 vol% alumina with DI water. After the addition of each ingredient, the suspension is mixed for 2 min at 1700 rpm.
4.2.3 Contact Angle Measurements

Static contact angle measurements are carried out by depositing 10 µL drops at an infill rate of 60 µL/min onto the surface of the dried precursor gel. The reported value of 59° ± 5° represents the average and standard deviation obtained from seven separate measurements.

4.2.4 Rheological Characterization

The rheological properties of the fluid, gel, and foam inks are characterized at 21°C using a controlled stress rheometer (Discovery HR-3 Hybrid Rheometer; TA Instruments). A 40 mm tapered cone geometry (2.005°, 56 µm truncation gap) is used for the fluid and gel, while a custom made 8-bladed vane (15 mm diameter, 38.5 mm height, 1.3 mm blade thickness, 4 mm gap) is used to quantify foam and pure colloidal ink properties. Flow sweeps are performed between $1 \times 10^{-3}$ and 400 s$^{-1}$. Oscillatory measurements are performed at 10 rad/s between $1 \times 10^{-4}$ - 10% strain.

4.2.5 Foam Ink Printability

Stable printing conditions are determined by extruding the foam through nozzles of varying diameter at different volumetric flow rates corresponding to an effective print speed ($v_{eff}$) ranging between 1 mm/s and 10 m/s. The extruded material was collected and analyzed (see 4.2.8). Effective print speed ($v_{eff}$) corresponds to the print speed required to deposit a filament of equivalent diameter to the nozzle of interest at a given ink volumetric flow rate: $v_{eff} = Q/(\pi \left(\frac{d}{2}\right)^2)$, where $Q$ is the volumetric flow rate and $d$ is the nozzle diameter.

4.2.6 Direct Foam Writing of Architected Cellular Ceramics

Foam-based structures are printed by depositing a foam ink, which is loaded into a 60 cc syringe and dispensed using a syringe pump (PHD Ultra; Harvard Apparatus), through either a 610 µm diameter (honeycombs) or 1.19 mm diameter (square bars) tapered nozzle (Nordson
The printed parts are formed by translating the ink-filled syringe in the prescribed path using a custom-built 3D printer (ABG 10000; Aerotech Inc.). All print paths are created by writing the appropriate G-code commands. The foam-based hexagonal and triangular honeycombs are printed at 48 mm/s and 24 mm/s, respectively. The bulk foam bars are printed at 30 mm/s with a flow rate of 2 mL/min into a 4 mm x 4 mm x 90 mm shape. The ink is printed onto a wax (Pure Petroleum Jelly; Vaseline) covered zirconia setter plate (Zircoa). Immediately after printing, the structures are placed into a box with controlled humidity and dried for at least 1 week, after which the structures are removed and allowed to dry at ambient conditions for at least 24 h. After drying, the structures are removed from the printing substrate and placed on a separate setter plate. Residual moisture is removed by heating at 70°C for 2 h, 90°C for 4 h, 110°C for 24 h with ramp rates of 0.5°C/min, after which binder burnout is performed according to the following schedule: 200°C for 20 h, 300°C for 20 h, 500°C for 20 h, 700°C for 20 h. Once binder removal is complete, the structures are sintered at 1500°C for 3 h. The respective heating and cooling rates are 1°C/min and 2°C/min in each case.

Nearly dense structures are printed by depositing the pure colloidal ink, which is loaded into a 30 cc syringe and dispensed using a positive displacement pump (Ultra 2800; Nordson EFD), through either a 610 μm diameter (honeycombs) or 1.36 mm diameter (bars) tapered nozzle using the same print set-up and substrate as the foam ink. The ink flow rate for both honeycombs is 0.53 mL/min. Hexagonal and triangular honeycombs are printed 36 mm/s and 18 mm/s, respectively. The print parameters and shape of the bulk foam bars are also used for the bulk nearly dense bars. Immediately after printing, the structures are placed into a box with controlled humidity and dried for 3 h, after which they are immersed in oil for two weeks or until they become rigid enough to handle. Following oil immersion, the honeycombs are dried at
ambient conditions for 24 h, and prefired and sintered following the same heat treatment process as described above for the foam structures.

4.2.7 Mechanical Characterization

Foam honeycombs and bulk foam bars as well as nearly dense honeycombs and bulk nearly dense bars are compressed at a constant crosshead speeds 0.025 mm/min, 0.05 mm/min, 0.12 mm/min (Model 4201; Instron) and 0.12 mm/min (Model 1321; Instron), respectively. Force measurements for the foam honeycombs and bulk foam bars, and their nearly dense counterparts, are performed with 500 N, 5000 N, and 50 kN load cells, respectively. Deflections for all structures except the nearly dense square bars are captured by a digital contact probe (GT2-P12K; Keyence) mounted in a custom bracket. The deflection of bulk nearly dense specimens is measured with a contact extensometer (2630-104; Instron). To minimize friction effects, both the bulk foam and bulk nearly dense compression specimens are in the form of square bars with an aspect ratio of at least eight. All specimens are ground such that the faces contacting the compression platens are flat and parallel within 5 μm. The vertical boundaries of each honeycomb are removed prior to testing to eliminate all non-cellular load bearing material. At least three specimens of each type are tested. Each specimen is tested three times. Reported averages and standard deviations are calculated from the mean stiffness value of each specimen. Modulus values for each test are obtained from linear regressions of the data. All tests are included in the reported results.

4.2.8 Porosity Measurements

Porosity is measured by image analysis using the systematic point count method (ASTM E562-08). At least 1000 grid points are analyzed over 19.5 mm² for each wet foam microstructure and at least 700 grid points over 1.5 mm² are analyzed for each sintered
architecture. Their mean pore size is obtained using the linear intercept method for two-phase materials (ASTM E112-13), where bubbles (or pores) are defined as the dispersed phase and the alumina suspension or sintered alumina matrix is defined as the continuous phase. For wet foams, at least 60 mm of lines are analyzed over 19.5 mm². For sintered specimens, 30 mm of lines were analyzed over 1.5 mm².

4.2.9 Density Measurements

To nondestructively measure the relative density of the printed and sintered honeycombs, in-plane images of the full honeycomb are taken against a black background and thresholded to obtain the areal coverage of the top surface of the printed structure ($\rho^*/\rho_{strut}$). The boundaries of the honeycombs are not included in the analysis, such that only the load bearing parts of the structures contribute to relative density. Images are taken from the top side of the honeycomb to minimize the contribution of the initially printed layers (~layers 1-3), which frequently had higher relative density compared to the rest of the layers. For bulk structures, the relative density is calculated according to their mass and volume, where the volume is determined using the Archimedes’ method. The net relative density of the honeycombs ($\rho^*/\rho_{s-theory}$) is calculated by

$$\left(\frac{\rho^*}{\rho_{strut}}\right) \left(\frac{\rho_{strut}}{\rho_s}\right) \left(\frac{\rho_s}{\rho_{s-theory}}\right) = \left(\frac{\rho^*}{\rho_{s-theory}}\right)$$

where $\rho_{s-theory}$ is the theoretical density of alumina (3.97 g/cm³), $\left(\frac{\rho_{strut}}{\rho_s}\right) = 1$ since the honeycomb microstructures are assumed to be the same as those of their respective bulk materials (i.e., sintered foam and nearly dense alumina), $\left(\frac{\rho_s}{\rho_{s-theory}}\right) = 0.903$ for nearly dense structures and $\left(\frac{\rho_s}{\rho_{s-theory}}\right) = 0.210$ for foam structures. $\left(\frac{\rho_s}{\rho_{s-theory}}\right) < 1$ for the nearly
dense material, while \( \left( \frac{\rho_s}{\rho_{s\text{-theory}}} \right) \) is equivalent to \( 1-\beta \) for foam structures, and \( \beta \) is microstructural porosity.

4.3 RESULTS AND DISCUSSION

4.3.1 Ink Design

Central to the fabrication of porous ceramic architectures is the design of a viscoelastic foam ink that embodies the requisite microstructural and rheological characteristics for direct foam writing. From a microstructural perspective, the wet ink must remain structurally stable over long time periods (> 1 week), possess modest bubble size (~10-50 \( \mu \text{m} \) in diameter), and maintain high air content (> 80%) after sintering. Reliably printing highly porous wet foams is inherently difficult due to the excess surface energy associated with the gas-liquid interface. If the gas-liquid interface is not well stabilized, bubble collapse will occur due to van der Waals attraction between adjacent interfaces, Ostwald ripening, or gravitational syneresis [74, 76, 77, 91, 125, 126]. Our foam ink is produced by mechanically frothing an aqueous suspension of partially hydrophobized alumina particles [91]. As introduced in Chapter 3, when the interfacial tension of the solid-liquid (\( \sigma_{sl} \)), liquid-gas (\( \sigma_{lg} \)), and solid-gas interfaces (\( \sigma_{sg} \)) is balanced such that the contact angle (\( \theta \)) of the particles and the solvent lies between the range of 14° and 90° calculated for 300 nm particles, the particles irreversibly and spontaneously adsorb onto liquid-gas (bubble) interfaces introduced during foaming (Figure 4.1B-C) [74, 76, 77, 91, 125, 126]. The adsorbed particles physically prevent van der Waals collapse and Ostwald ripening, and for sufficiently attractive interparticle interactions, arrest drainage, yielding a stable foam microstructure that retains its characteristic bubble content and size over long times [14]. Direct imaging of wet foams stabilized by alumina particles (300 nm in diameter with a measured contact angle of 59° ± 5°) immediately after production (0 days) and aging (7 days) reveals a
total entrained porosity of 54.3 ± 2% and 54.8 ± 1%, respectively, with a respective bubble size of 24.0 ± 1.4 μm and 22.9 ± 1.3 μm (Figure 4.1D-E). After drying and sintering, the total porosity within the ceramic foam microstructure increases to 85 ± 3% due to densification of the cell walls, while the characteristic pore size remains essentially unchanged (23.7 ± 1.4 μm) from the wet foam state (Figure 4.1F). Notably, the cell walls, which are sub-micron in thickness, can be as thin as a single grain (Figure 4.1G).

**4.3.2 Ink Rheology and Printability**

To facilitate printing, wet foam inks must exhibit significant shear thinning to allow extrusion through fine nozzles as well as sufficiently large storage modulus, $G'$, and shear yield strength, $\tau_y$, to retain their filamentary shape upon exiting the nozzle. The rheological properties of the ink at different stages of the formulation process are shown in Figure 4.2. First, a charge stabilized, aqueous dispersion of alumina particles (35 vol% solids) that are partially hydrophobized using the surfactant, butyric acid, is prepared at pH < 3. The colloidal fluid is strongly shear thinning, as evidenced by a pronounced decrease in its apparent viscosity from 900 Pa·s to 0.1 Pa·s as the shear rate increases from $10^{-3}$ s$^{-1}$ to $10^2$ s$^{-1}$. This flow behavior ensures that the colloidal fluid can be easily foamed at shear rates above $10^1$ s$^{-1}$, i.e., its low viscosity does not impede aeration. However, since its plateau $G'$ (~$10^2$ Pa) and $\tau_y$ (~1 Pa) are low, gravitational syneresis occurs after foaming (Figure 4.3). To impart structural stability, a weakly attractive interaction is induced between colloidal particles by increasing the solution pH~5, thereby reducing the particle charge. The resulting colloidal gel possesses an apparent viscosity that is equivalent to the colloidal fluid at shear rates above $10^1$ s$^{-1}$, facilitating aeration. Moreover, its plateau $G'$ (~$10^4$ Pa) and $\tau_y$ (~3 Pa) are now sufficiently high to prevent syneresis (Figure 4.1D-E). Upon foaming, the apparent viscosity of the final ink increases by an order of
magnitude over all shear rates investigated, and a concomitant increase in the plateau $G' (~5 \cdot 10^4 \text{Pa})$ and $\tau_y (~10^2 \text{Pa})$ is observed. Further increases in pH preclude effective aeration during foaming. For instance, CGFs produced from gels at pH = 6 have less than 30% porosity (Figure 4.3).
Figure 4.2: **Ink rheology and printability.** (A) Plot of apparent viscosity as a function of shear rate and (B) storage and loss moduli as a function of shear stress for various processing steps in the foam ink formulation process. (C) Processing map for direct foam printing, which denotes regions of stable (green) and unstable (red) printing with the white box highlighting parameters used to print hexagonal and triangular foam-based honeycombs. [Note: Unstable printing arises due to one of three failure mechanisms: (1) foam ink clogging in fine nozzles (light red), (2) foam ink drying at the nozzle tip at low printing speeds (red), or (3) bubble coalescence at high printing speeds and fine nozzle sizes (dark red).]
Figure 4.3: Foam processing. (A) Optical image of the foam precursor solution (colloidal fluid, pH< 3) after foaming. Air is introduced during foaming, but gravitational syneresis immediately destabilizes the foam. (B) Image of the colloidal gel (pH 6) before foaming, and (C) foam microstructure obtained after foaming. (Scale bar = 500 μm). (Note, the bubble content and characteristic size depends strongly on pH, where 54.3 ± 2% porosity and 24.0 ± 1.4 μm pores are entrained at pH 5 compared to 29.2 ± 2% porosity and 10.8 ± 1.0 μm pores at pH 6) (D) SEM image of the sintered ceramic foam microstructure (shown in Figure 4.1) after printing through a 610 μm nozzle at a flow rate of 1mL/min. (Scale bar = 100 μm).

Importantly, our foam inks readily flow through nozzles (diameter ≥ 200 μm) at volumetric flow rates equivalent to effective print speeds from 10 mm/s up to 10 m/s, as shown in Figure 4.2C. Particle clusters within the weakly attractive colloidal gel undergo clogging within finer nozzles (< 200 μm in diameter) leading to the cessation of ink flow [107]. For nozzle sizes that exceed approximately 400 μm, the wet foam microstructure is preserved, i.e., bubbles do not coalesce, at effective print speeds as high as 10 m/s (Figure 4.4). However, ink drying at the nozzle tip (< 800 μm in diameter) occurs for the lowest printing speed (1 mm/s) investigated, and the foam coalesces for nozzle diameters between 200-400 μm at effective print speeds exceeding 10³ mm/s. Given our prior observations of direct writing of concentrated colloidal gels, we believe that a slip layer exists at the nozzle wall-foam ink interface, which facilitates plug flow through the nozzle thereby preserving the wet foam microstructure (23).
Figure 4.4: Printing effects on wet foam microstructure. (A) The initial foam microstructure prior to printing. The foam microstructures after printing at (B) 40 mm/s through a 610 μm nozzle, which are similar to the printing parameters used for creating the foam-based hexagonal and triangular honeycombs, (C) 10^3 mm/s through a 200 μm diameter nozzle, and (D) 10^4 mm/s through a 410 μm diameter nozzle. (Scale bars = 500 μm). In all cases, the overall porosity and characteristic pore size of the printed foams (B-D) are nearly equivalent to the initial values (A).

4.3.3 Direct Foam Writing of Ceramic Honeycombs

To demonstrate direct foam writing, we printed the colloidal gel foam ink through a 610 μm diameter nozzle at a constant volumetric flow rate of ~1 mL/min to create bending dominated hexagonal, and stretching dominated triangular, honeycombs composed of bending dominated closed foam struts (Figure 4.5). Note, these printing parameters reside within the stable printing regime delineated in Figure 4.2C. The printed hexagonal honeycombs are 80 mm wide x 40 mm tall x 7.5 mm thick, while the triangular honeycombs are 83 mm wide x 53 mm tall x 7.3 mm thick. These sample dimensions are used to ensure equivalent relative density between honeycombs composed of the same strut microstructure, but different cell geometries. As a control, we also developed a pure colloidal ink without bubbles that possesses the required rheological characteristics for direct ink writing (Figure 4.6). Using this ink, we create honeycombs with nearly dense alumina struts (Figure 4.7). After printing, the honeycombs are dried under controlled humidity, bisque fired to remove organic additives, and sintered at 1500°C. The observed shrinkage during drying and sintering yields highly porous hexagonal and
triangular ceramic honeycombs, whose dimensions are nominally 62 mm x 32 mm x 5.5 mm and 65 mm x 41 mm x 5.5 mm, respectively. Both printed geometries have relative densities of \( \rho^*/\rho_{\text{strut}} \sim 28\% \) and contain struts with \( \sim 79\%-85\% \) porosity (\( \rho_s/\rho_{s,\text{theory}} \sim 15\%-21\% \) relative density), yielding a net relative density of \( \rho^*/\rho_{s,\text{theory}} \sim 6\% \), where \( \rho^* \), \( \rho_{\text{strut}} \), \( \rho_s \), and \( \rho_{s,\text{theory}} \) represent the densities of the printed honeycomb, the strut, the bulk material composing the honeycomb (i.e., sintered foam or nearly dense alumina) and theoretically dense alumina, respectively. The nodes of each printed structure reveal seamless integration of printed filaments (Figure 4.5C,G), whose foam microstructure remains consistent between different honeycombs (Figure 4.5D,H). The printing process has a negligible effect on the foam microstructure within the filaments (Figure 4.3-4.4). However, a dense skin is observed at the filament surface (Figure 4.8), akin in morphology and thickness to the surface layer observed for the bulk cast foam (Figure 4.9), as a consequence of surface area minimization [142].
Figure 4.5: 3D porous ceramic honeycombs. (A, B) Representative sintered hexagonal honeycomb. (Scale bar = 5 mm). (C) Image of one node of the hexagonal honeycomb and (D) the resulting microstructure. (Scale bars = 500, 100 μm). Representative sintered triangular honeycomb (E, F). (Scale bar = 5 mm). (G) Image of one node of the triangular honeycomb and (H) the resulting microstructure. (Scale bars = 500 μm and 100 μm, respectively).
Figure 4.6: Pure colloidal ink rheology and microstructure after sintering. (A) Storage and loss moduli as a function of shear stress for the pure colloidal ink compared to the foam ink and its precursors. (B-C) Representative SEM images of the nearly dense ceramic microstructure after sintering at lower and higher magnification, respectively. (Scale bars = 50 µm and 5 µm, respectively).
Figure 4.7: Optical images of representative printed nearly dense (A, B) hexagonal and (C, D) triangular honeycombs after sintering. (Scale bars = 5mm).
**Figure 4.8: Structure of printed foam filaments.** Cross-sectional images of (A) foam honeycomb border, in which each printed foam filament possesses (B) a dense, thin skin surrounding (C, D) a highly porous, closed-cell interior. (Scale bars =1000 μm, 1000 μm, 250 μm, and 50 μm, respectively).

**Figure 4.9: SEM image of the external surface and interior of a molded and sintered foam structure, which reveals that skin formation is not unique to direct foam writing.** (Scale bar = 200 μm).
4.3.4 Mechanical Properties

The sintered hexagonal and triangular ceramic honeycombs composed of both nearly dense struts (bending and stretching, respectively) and foam struts (bending-bending and stretching-bending, respectively) are non-destructively compressed in-plane to evaluate the influence of their printed microstructure and cell geometry on stiffness. Representative elastic stress-strain curves for each bulk material and honeycomb type are shown in Figure 4.10-4.11. The elastic behavior of the honeycombs is well predicted by:

\[
\frac{E^*}{E_{\text{strut}}}=B\left(\frac{\rho^*}{\rho_{\text{strut}}}\right)^b
\]  

(4.1)

where \(E^*\) is the honeycomb stiffness, \(E_{\text{strut}}\) is the strut stiffness, \(\rho^*\) is the honeycomb density, \(\rho_{\text{strut}}\) is the strut density, and \(B\) and \(b\) are unit cell dependent loading constants. Note, \(B = 3/2, 1/3\) and \(b = 3, 1\) for hexagonal and triangular honeycombs, respectively [29, 30]. Based on the relative densities of the nearly dense honeycombs (\(\rho_{\text{hex}}^*/\rho_{\text{strut-s}} = 0.287 \pm 0.003, \rho_{\text{tri}}^*/\rho_{\text{strut-s}} = 0.293 \pm 0.003\) where \(s\) corresponds to the nearly dense ceramic), the bending dominated hexagonal honeycombs should be 36% as stiff as the stretching dominated triangular ones. The measured elastic moduli of nearly dense hexagonal and triangular honeycombs are 9.9 ± 1.8 GPa and 27.4 ± 1.0 GPa, respectively, which is within 1% of the predicted relative difference (Table 4.1). Both structures have knockdown factors less than 20% from their theoretical values based on the measured modulus of 344 ± 27 GPa for nearly dense alumina, which is determined by elastically compressing square bars.
Figure 4.10: Mechanical properties of the 3D ceramic architectures. (A) Stress as a function of strain (confined to the elastic region) for all printed structures. (B) Elastic modulus as a function of specimen hierarchy. (C) Plot of elastic modulus as a function of density that compares our printed architectures to other bulk alumina foams [23–25] and 3D periodic lattices produced by light-based 3D printing [26–28].
Figure 4.11: Elastic stress as a function of strain for (A) nearly dense bars, (B) nearly dense triangular honeycombs, (C) nearly dense hexagonal honeycombs, and (D) foam bars, (E) triangular foam honeycombs, and (F) hexagonal foam honeycombs.

Table 4.1: Summary of Material Properties

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Geometry</th>
<th>(\frac{\rho^*}{\rho_{\text{strut}}})</th>
<th>(\frac{\rho_{\text{strut}}}{\rho_s})</th>
<th>(\frac{\rho_s}{\rho_s,\text{theory}})</th>
<th>(\rho) [kg/m^3]</th>
<th>(E_{\text{strut}}) [GPa]</th>
<th>(E^*), Theory [GPa]</th>
<th>(E^*), Measured [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nearly Dense</td>
<td>Bulk</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>344 ± 27</td>
</tr>
<tr>
<td></td>
<td>Hexagonal Honeycomb</td>
<td>0.287 ± 0.003</td>
<td>0.903 ± 0.04</td>
<td>0.259</td>
<td>1029</td>
<td>344 ± 27</td>
<td>12.2</td>
<td>9.9 ± 1.8</td>
</tr>
<tr>
<td></td>
<td>Triangular Honeycomb</td>
<td>0.293 ± 0.003</td>
<td>0.265</td>
<td>1050</td>
<td>33.6</td>
<td>27.4 ± 1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foam</td>
<td>Bulk</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>21.8 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>Hexagonal Honeycomb</td>
<td>0.275 ± 0.01</td>
<td>0.210 ± 0.01</td>
<td>0.058</td>
<td>229</td>
<td>21.8 ± 1.2</td>
<td>0.68</td>
<td>1.36 ± 0.06</td>
</tr>
<tr>
<td></td>
<td>Triangular Honeycomb</td>
<td>0.288 ± 0.01</td>
<td>0.060</td>
<td>240</td>
<td>2.09</td>
<td>3.04 ± 0.26</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Equivalent compression measurements are carried out on ceramic honeycombs composed of foam struts. From their printed relative densities ($\rho_{\text{hex}}^*/\rho_{\text{strut-f}} = 0.275 \pm 0.01$, $\rho_{\text{tri}}^*/\rho_{\text{strut-f}} = 0.288 \pm 0.01$, where $f$ corresponds to foam), and the measured foam modulus of $21.8 \pm 1.2$ GPa, which is determined by elastically compressing square bars of closed-cell alumina foam, one predicts elastic moduli of 0.68 GPa for the hexagonal foam honeycomb and 2.09 GPa for the triangular foam honeycomb, indicating the bending dominated hexagonal structure should exhibit 33% of the stiffness of the stretching dominated triangular honeycomb. The measured values are $1.36 \pm 0.06$ GPa and $3.04 \pm 0.26$ GPa for each honeycomb, respectively. Increased stiffness for both architectures relative to model predictions may stem from underestimating $\rho^*/\rho_{\text{strut-f}}$ due to thickness gradients in the cell walls (Figure 4.12). The initially printed layers (~layers 1-3) frequently had somewhat higher relative densities due to substrate effects. Moreover, strut thickness, and thickness gradient within a strut, can vary within a given honeycomb (Figure 4.12). Variable strut thickness between layers is not captured in the relative density measurement, which may lead to increased honeycomb stiffness compared to predictions based on the honeycomb density and properties of the solid foam.
Figure 4.12: Optical images of defects observed in the printed ceramic architectures. (A) Representative image of a through thickness cross-section of one of the sintered foam hexagonal honeycombs. (B, C, D) The struts bisected by the cross-sectional cut show that the layers printed closer to the substrate can be thicker than the layers printed further away from the substrate. Strut thickness, and thickness gradient within a strut, can vary within a given honeycomb. For instance, the strut in (B) is thicker than (C) and (D), while (B) and (C) also show stronger thickness gradients compared to (D). Variable strut thickness between layers is not captured in the relative density measurement, which may lead to increased honeycomb stiffness compared to model predictions based on the honeycomb density and properties of the solid foam. (Scale bars = 1 mm). Furthermore, printed architectures may contain (E) stacking faults and (F, G) wall bowing. (Scale bars = 1 mm, 2.5 mm, and 2.5 mm, respectively).
Additionally, the hexagonal honeycomb modulus is 12% stiffer than expected relative to the triangular honeycomb. This observed difference likely arises due to the relative importance of defects, e.g. wall thickness variations, offset stacking between printed layers, and bent struts (Figure 4.12), on their stiffness. Such defects would have a more pronounced effect on the stiffness of triangular honeycombs, as their stretching behavior would be disrupted thereby reducing their stiffness, compared to the hexagonal honeycombs [22]. The ratio of the elastic moduli of the honeycombs with different strut microstructures illustrates the effect of strut hierarchy on elastic modulus, and should vary according to $E_{\text{hex-f}}^*/E_{\text{hex-s}}^* = 0.056$ and $E_{\text{tri-f}}^*/E_{\text{tri-s}}^* = 0.062$. However, the measured ratios of $E_{\text{hex-f}}^*/E_{\text{hex-s}}^* = 0.137$ and $E_{\text{tri-f}}^*/E_{\text{tri-s}}^* = 0.111$ are roughly double these predicted values, again likely due to underestimating $\rho^*/\rho_{\text{strut-f}}$.

Nevertheless, the actual difference in stiffness between identical honeycomb geometries with different strut microstructures is nearly an order of magnitude in each case (Figure 4.10B-C).

Direct foam writing produces triangular foam honeycombs with higher specific stiffness ($> 10^7 \text{ Pa/(kg/m}^3)$ and lower density (~200 kg/m$^3$) than bulk alumina foams produced by gelcasting particle-stabilized foams [23], freeze-casting [24], or capillary suspensions [25] (Figure 4.10C). Notably, our structures also possess superior specific stiffness at similar relative density compared to more exotic alumina lattices produced by other 3D printing methods [26–28], without the need for template removal or secondary coating steps. While our experiments have focused on printing and characterizing hexagonal or triangular cells composed of a single foam microstructure and lattice density, the architecture-property space realizable via direct foam writing can be substantially broadened by varying: (1) the bubble volume fraction within the foam ink, and hence, microstructural porosity ($\beta$), (2) strut aspect ratio ($t/l$), or (3) cell geometry,
represented by a constant, \( C \). For our unit cell geometries, the effects of these parameters on relative density are given by:

\[
\left[ \frac{\rho^*}{\rho_s} \right] = C (1 - \beta) \left[ \frac{t}{l} \right]
\]

(4.2)

where \( t \) is the strut thickness, \( l \) is the strut length, and \( C \) is \( 2/\sqrt{3} \) for hexagonal honeycombs and \( 2\sqrt{3} \) for triangular honeycombs [30].

One current limitation of direct foam writing is the inability to pattern out-of-plane spanning features, such as octet trusses. However, this technique is well suited for printing 3D woodpile lattices composed of foam struts [50]. As an alternate motif, we created 3D woodpile lattices (Figure 4.13) composed of hollow core-foam shell struts using a coaxial printhead in which the CGF ink (shell) is co-extruded with a fugitive wax core [40]. These hollow core-foam shell struts mimic natural structures, such as stems or quills, that rely on cross-sectional variations in material placement and microstructure to achieve their desired functionality [2].

![Figure 4.13: Natural stem and printed 3D core-shell architectures.](image)

(A) Cross-sectional image of a grass stalk (reprinted from Ref. 40 with permission). Top-down (B) and end-on images (C) of a representative woodpile structure composed of filaments with foam shells and hollow cores (D). (Scale bars = 250 \( \mu \)m, 1000 \( \mu \)m, 1000 \( \mu \)m, and 500 \( \mu \)m, respectively).
4.4 CONCLUSIONS

In summary, we have created architected porous ceramics via direct writing of colloidal gel foams and characterized their mechanical properties. Solely by varying architecture (e.g., unit cell type and strut porosity), we systematically tuned the elastic modulus between ~ 1 GPa for hexagonal honeycombs composed of foam struts to 27 GPa for triangular honeycombs composed of nearly dense struts. These ceramic honeycombs possess greater specific stiffness (> $10^7$ Pa/(kg/m$^3$)) compared to micro- and nanoscale lattices of similar relative densities produced by other additive manufacturing methods. Given the generality and scalability of direct foam writing, it should be straightforward to pattern other ceramic, metal, and polymer foam-based inks, with either closed or open cellular microstructures, to further expand the applications realizable by this nascent approach.
CHAPTER 5

CONCLUSIONS

My dissertation focused on developing an extrusion-based 3D printing method, direct foam writing (DFW), to create multi-scale cellular ceramics inspired by hierarchical architectures found in nature (wood and stems). Specifically, colloidal gel foam (CGF) inks that contain dispersed bubbles interconnected by a space-filling, attractive alumina particle network were created, and their structure – elasticity relationships were established for the first time. Highly stable CGFs possess closed cell microstructures that persist after printing through fine nozzles (diameter > 200 μm). Lightweight hierarchical ceramics in the form of honeycombs with closed-cell foam walls were produced by DFW. By controlling the CGF microstructure and honeycomb architecture, we tailored their density, deformation mode, and stiffness over a broad range of values. Importantly, these multi-scale architectures exhibit specific stiffness exceeding $10^7$ Pa/(kg/m$^3$), which is higher than that reported for both bulk foams and more complex 3D lattices produced by light-based 3D printing. DFW represents a scalable route for manufacturing multi-scale cellular materials over large build volumes from myriad material chemistries, including other ceramics, polymers and metals, without the need for photopolymerization.

5.1 PRINCIPAL FINDINGS

The principal findings of my PhD research are summarized below:

1) Modular CGF ink design for 3D printing architected cellular ceramics

DFW requires an ink with a stable, tailorable cellular microstructure that affords material flexibility and possesses the requisite rheological behavior to pattern 3D architectures.

We developed a CGF ink that meets these criteria. Specifically, our viscoelastic CGF ink
is composed of closed cell foam stabilized by an aqueous alumina colloidal gel, whose cellular microstructure persists after extrusion through fine nozzles (> 200 μm in diameter) at effective print speeds up to 1 m/s. Upon drying and sintering, the CGF is transformed into macroporous alumina that contains spherical pores (~ 20-30 μm) and greater than 80% porosity. Our modular CGF inks can readily be expanded to other ceramics, polymers, metals, and even composite systems, to create open or closed cell foams.

2) CGF structure - elasticity evolution

Particle hydrophobicity, suspension pH, colloid volume fraction, and foaming intensity influence the structure and elasticity of CGFs. Foam characteristics remain virtually unchanged for surfactant concentrations required to produce stable foams. However, changing particle hydrophobicity by altering surfactant chain length leads to a four-fold increase in CGF specific surface area, and a three-fold increase in shear elastic modulus ($G'_f$). Changing the stiffness of the colloidal gel over the tested pH (pH = 4.5 - 5.5) and solids loading ($\phi_c = 0.25 - 0.45$), leads to CGFs with specific interfacial area similar to the foams of varying particle hydrophobicity. However, their elasticity, $G'_f$, varies by over one order of magnitude. Increased foaming intensity for a given CGF formulation concomitantly increases specific interfacial area and elasticity.

3) Stable processing window for CGF materials

Colloidal particles adequately stabilize foams when they are sufficiently hydrophobic to adsorb onto the entrained liquid-gas (bubble) interfaces and present in adequate quantity to form a gel in the continuous phase that is strong enough to arrest creaming. Stable foams with $\phi_c = 0.35$, surfactant concentration between 0.3 μmol/m² - 0.9 μmol/m² and
appropriate alkane chain length \( (X = 5 - 7) \) were attained for \( \text{pH} > 4.5 \), which corresponds to \( G'_c > 7.6 \times 10^1 \) Pa. For a given particle hydrophobicity, specific interfacial area is determined by the stiffness of the precursor colloidal gel and the mechanical aeration energy. Maximum specific interfacial area occurs when the gel is stiff enough to incorporate small bubbles without sacrificing total air content. For the foaming method used, the optimal gel stiffness is \( 4.6 \times 10^4 \) Pa (\( \text{pH} = 5.5 \)), which leads to a foam ink with a specific interfacial area of \( 233 \text{ mm}^2/\text{mm}^3 \). At the same foaming intensity, precursor gels with higher stiffness had comparable bubble size, but lower bubble volume fraction, while less stiff gels led to foams composed of larger bubbles at similar bubble content. For precursor gels with excessively high stiffness (i.e., \( G'_c > 1.8 \times 10^5 \) Pa) no air could be entrained, while for \( G'_c < 7.6 \times 10^1 \) Pa all foams creamed. We expect similar trends to exist for CGF precursors with different solids loadings, except the cut-off for stable foams would shift to higher \( \text{pH} \) values for \( \phi_c < 0.35 \) and lower \( \text{pH} \) values for \( \phi_c > 0.35 \).

4) **CGF elasticity scales nearly linearly with specific interfacial area**

We observed significant increases in CGF elasticity compared to the colloidal gel alone, even for \( \phi_b < 0.20 \). We hypothesize that this behavior arises due to the ability of the colloidal gel to link entrained bubbles forming a percolating bubble network far below \( \phi_{cp} \). As interfacial area is entrained within the system, more particles occupy bubble interfaces, and the bubble network becomes increasingly connected. The increased bubble interfacial area enables a proportionally larger amount of stress to be transmitted, increasing the elasticity of the system. Notably, their shear elastic modulus increases nearly linearly with the amount of specific interfacial area regardless of surfactant length, \( \text{pH} \), or solids loading. We note that specific interfacial area and \( G'_f \) are also linearly
related in particle-free dry foams, where the bulk elastic response is determined by the
elasticity of the bubble interfaces [112, 113]. We believe our system is akin to those
systems, except the stress transfer between dispersed entities in CGFs occurs through the
continuous colloidal gel rather than through interfacial deformation.

5) **Direct foam writing enables fabrication of architected cellular ceramics**

By combining the material placement characteristics of direct ink writing with the
microscale cellular features entrained in CGF inks, direct foam writing enables one to
rapidly pattern materials into hierarchical cellular solids.

6) **Multi-length scale control of material architecture enables tailorable elasticity and**

**broadens materials space coverage**

By employing DFW to create bending dominated hexagonal and stretching dominated
triangular honeycombs composed of foam or nearly dense cell walls, we deterministically
defined the density and stiffness of hierarchical cellular ceramics. We created porous
architectures with densities ranging from 229 – 1050 kg/m³ and stiffnesses between 1.36
- 27.4 GPa. When compared to bulk alumina, this property range represents an extension
of material space greater than one order of magnitude in density and two orders of
magnitude in elastic modulus.

7) **Combining cellular structures across multiple length scales enables unprecedented**

**specific stiffness**

Stretching dominated macroscale honeycomb architectures composed of low density
closed cell alumina foams enable hierarchical cellular ceramics with specific stiffness
exceeding 10⁷ Pa/(kg/m³). Notably, our materials are more specifically stiff compared to
either bulk alumina foams or 3D micro- or nanoscale lattices while maintaining
comparable or lower density and without requiring template removal or secondary processing steps.

5.2 CHALLENGES AND OPPORTUNITIES

My Ph.D. research has opened a new avenue for fabricating hierarchical cellular solids. This nascent approach has both challenges and opportunities, as described below.

1) Polydisperse foam microstructures

Introducing entrained air via mechanical aeration creates a polydisperse bubble network within CGFs. Their polydisperse nature may prevent their implementation in applications where strict pore size control (e.g., filters) or interfacial area control (e.g., catalyst supports) are needed. Other aeration methods such as in situ gas formation [143] and bubble blowing [144] may enable more homogeneous bubble populations to be incorporated.

2) 3D imaging of CGFs

CGFs are characterized by relatively high solids loading in the continuous phase and possess substantial liquid-air interfacial area. Both of these characteristics hinder in situ imaging of wet CGFs. If one could use 3D imaging techniques, such as confocal laser scanning microscopy, new insights regarding bubble stabilization and network formation mechanisms could be obtained [72, 95, 101, 107, 114]. This information could be used to validate our proposed CGF structure-elasticity relationship. Moreover, additional studies on CGF yielding and flow behavior would be possible, which may enable new fundamental understanding of this nascent class of soft matter.
3) **Drying printed foams**

In the current embodiment, hierarchical cellular ceramics produced by DFW must dry prior to sintering. Because the printed structures have limited green strength, they are prone to substantial warping due to differences in evaporation rates from the top and bottom surfaces. Moreover, even if drying is carried out uniformly, long drying times (~1 week) are required to prevent cracking. Developing new foam inks that facilitate faster drying would substantially enhance the scalability and flexibility of DFW. To enhance their green strength, one could add a monomer to the CGF precursor that would enable post-deposition cross-linking [15, 91, 145, 146] or identify alternative binders [61]. However, one must take great care to ensure that any new additives do not impede the foaming process or lead to less stable foams.

4) **Printed geometries are not truly arbitrary 3D shapes**

DFW is well suited to patterning materials that possess in-plane spanning elements, enabling honeycombs and woodpile structures [33]. However, it is impossible to produce 3D lattices (e.g., octet trusses) with out-of-plane spanning features. To create 3D unit cells, a support material or on-the-fly setting mechanism must be integrated. Two particularly interesting approaches are embedded 3D printing and on-the-fly solidification. In the former case, the CGF ink would be patterned within a viscoelastic fugitive matrix that supports the printed geometry in all directions, allowing nearly arbitrary shapes to be fabricated [147, 148]. After patterning, the CGF would dry/set within the support matrix, the matrix would be removed, and the resulting 3D part would be sintered. Alternatively, one could incorporate a photo- or thermo-sensitive monomer that can be cross-linked on-the-fly during printing. If the polymerization kinetics occur
on the deposition timescale, the CGF ink could be “set” during direct writing, allowing a broader range of printed architectures to be realized [149, 150].
REFERENCES


