3D printing engineered materials via integration of ultrasound directed self-assembly with stereolithography

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Overview

- Introduction
- Background
- Dynamics of a particle in an ultrasound wave field
- Ultrasound directed self-assembly in 1D
- Ultrasound directed self-assembly in 2D
- Ultrasound directed self-assembly with stereolithography
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Introduction: Engineered materials

- **Engineered materials based on nano- or microparticles embedded in a matrix material:** achieve unique physical properties due to the material properties, geometry, and arrangement of the particles

- **Applications:** cloaking, subwavelength imaging, electromagnetic shielding, ultra-high strength/weight structures, embedded electrical wiring

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**Negative-index optical materials**

**Negative-index acoustic materials**

**High-strength and conductivity composite materials**

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Introduction: Ultrasound directed self-assembly

- **Critical problem:** How to create user-specified patterns of particles over a macroscale area and volume

- **Proposed solution:** Ultrasound directed self-assembly (DSA)
Introduction: Ultrasound directed self-assembly

- **Critical problem:** How to create user-specified patterns of particles over a macroscale area and volume

- **Proposed solution:** Ultrasound directed self-assembly (DSA)
Introduction: Research objective

• **Objective 1**: Derive a dynamic model for the trajectory of a spherical particle in a fluid medium subjected to a standing ultrasound wave field

• **Objective 2**: Derive an ultrasound DSA method to manipulate a single particle and organize multiple particles into a user-specified pattern

• **Objective 3**: Integrate ultrasound DSA with stereolithography (SLA) for 3D printing of engineered materials
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Background: Directed self-assembly

**Directed self-assembly**: The process by which discrete components spontaneously organize due to interactions between the components and their environment, driven by internal or external forces [4]

<table>
<thead>
<tr>
<th>Templated</th>
<th>Template-free</th>
<th>External field</th>
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<tbody>
<tr>
<td>Soft templates</td>
<td>Hard templates</td>
<td>Source: [5]</td>
</tr>
<tr>
<td>0.5 μm</td>
<td>50 nm</td>
<td>Source: [6]</td>
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<tr>
<td>Limitation:</td>
<td>Limitation:</td>
<td>Limitation:</td>
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<tr>
<td>• Soft template sizes on the order of nm-μm</td>
<td>• Patterns are determined by particles and capping molecules</td>
<td>• Electric and magnetic techniques require ultra-high field strengths, and/or conductive and ferromagnetic particles</td>
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<tr>
<td>Hard templates</td>
<td>Source: [7]</td>
<td>Source: [8]</td>
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<tr>
<td>100 nm</td>
<td>250 μm</td>
<td></td>
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<tr>
<td>Soft templates</td>
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<td>Source: [9]</td>
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<tr>
<td>1.5 mm</td>
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<td></td>
</tr>
</tbody>
</table>

Background: Ultrasound DSA

• Acoustic radiation force:
  \[ \mathbf{f} = -\nabla U \]

• Radiation potential:
  \[ U = 2\pi r_p^3 \left( \frac{1}{3} \beta_f \Phi_\beta \left\langle |p|^2 \right\rangle - \rho_f \Phi_\rho \left\langle |\mathbf{u}|^2 \right\rangle \right) \]

• Acoustic contrast factors:
  \[ \Phi_\beta = 1 - \frac{\beta_p}{\beta_f}, \quad \Phi_\rho = \frac{\rho_p - \rho_f}{2\rho_p + \rho_f} \]
  \[ \Phi = \Phi_\beta + 3\Phi_\rho \]

  • \( p \): Incident ultrasound wave field (pressure)
  • \( \mathbf{u} \): Fluid velocity
  • \( r_p \): Particle radius
  • \( \lambda \): Ultrasound wavelength
  • \( \rho \): Density
  • \( \beta \): Compressibility
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Dynamics of a particle in an ultrasound wave field: Problem statement

- **Critical problem:** Model the forces acting on a spherical particle in a standing ultrasound wave field and analyze the transient and steady-state particle motion.

- Spherical particle motion is driven by acoustic radiation force $\mathbf{f}$ and drag force $\mathbf{f}_d$.

- **Existing models:**
  - Only consider drag force due to particle motion in quiescent fluid medium.
  - Only analyze relative magnitudes of forces.

- **Objective:** Model the dynamics of a spherical particle in a standing ultrasound wave field and analyze the particle trajectory as it is driven to the node of the ultrasound wave field.
Dynamics of a particle in an ultrasound wave field: Theoretical model

- **Dynamic model**

  \[
  m\ddot{x} - C_r \sin 2kx - C_s (\bar{u} - \dot{x}) - C_o (\bar{u} - \dot{x})|\bar{u} - \dot{x}| = 0
  \]

  **Nonlinear equation of motion**

  **Linearized equation of motion**

  \[
  m\ddot{x} - 2kC_r x + C_s \dot{x} - F_{td}(x, \dot{x}, t) = 0
  \]

  \[
  F_{td}(x, \dot{x}, t) = C_s \bar{u} + C_o (\bar{u} - \dot{x})|\bar{u} - \dot{x}|
  \]

  Particle inertia

  Particle Acoustic radiation force

  Drag force

  Time-independent drag

  Time-dependent drag

  Particle in a fluid medium

  Reservoir

  Fluid medium

  Particle

  Node

  \( p(x,t) \)

  \( x_0 \)

  \( x_s \)

  Ultrasound transducer

  **Acoustic radiation force coefficient**

  \[
  C_r = 4\rho_f \pi r_p^2 \rho_0^2 \left[ \Phi k r_p + O(k r_p^3) \right]
  \]

  **Stokes’ drag coefficient**

  \[
  C_s = 6\pi \mu_f r_p
  \]

  **Oseen’s drag coefficient**

  \[
  C_o = 9/4\pi \rho_f r_p^2
  \]

  **Time-dependent drag**

  \( x \): Particle position

  \( \bar{u} \): Mean fluid velocity at particle surface

  \( \rho_f \): Fluid density

  \( \mu_f \): Fluid viscosity

  \( r_p \): Particle radius

  \( m \): Particle mass

  \( \Phi \): Acoustic contrast factor
Dynamics of a particle in an ultrasound wave field: Transient behavior

- Simulate the trajectory of a particle in an ultrasound wave field and analyze transient behavior
- Transient particle behavior depends on the force ratio $K_1$

\[
K_1 = \frac{p \rho \Phi kr^2}{\rho_f \mu c_f^3} \approx \frac{\text{Acoustic radiation force}}{\text{Time-independent drag force}}
\]

**Simulated particle trajectories**

- $K_1 = 3.31 \times 10^{-5}$
- $K_1 = 1.33 \times 10^{-4}$
- $K_1 = 1.26 \times 10^{-2}$
- $K_1 = 8.60 \times 10^{-2}$

**Transient response characteristics**

- Settling time $T_s$
- Percent overshoot $M_p$

\[
\log(T_s) \quad \log(M_p) \quad \log(K_f)
\]

- $\Phi_1 = 0.74$ - 304 SS in water
- $\Phi_2 = 0.12$ - Polystyrene in water
- $\Phi_3 = -27.56$ - Cork in water
Dynamics of a particle in an ultrasound wave field: steady-state behavior

- Simulate the trajectory of a particle in an ultrasound wave field and analyze steady-state response
- Particle oscillates around $x_s$ at steady-state

Steady-state particle behavior depends on two force ratios, $K_1$ and $K_2$

$$K_1 = \frac{p_a^2 \Phi kr_p^2}{\rho f \mu c_f^3} \approx \frac{\text{Acoustic radiation force}}{\text{Time-independent drag force}}$$

$$K_2 = \frac{\mu + u_a \rho_f r_p^2}{\omega \rho f r_p^2} \approx \frac{\text{Time-dependent drag force}}{\text{Particle inertia}}$$

$\Phi_1 = 0.74$
$\Phi_2 = 0.12$
$\Phi_3 = -27.56$
Dynamics of a particle in an ultrasound wave field: Conclusion

• We analyze the dynamics of a particle submerged in a fluid medium, driven to the node of a standing ultrasound wave by acoustic radiation force

• We characterize the transient particle behavior:
  ▪ Increasing the ratio between the acoustic radiation force and the time-independent drag force ($K_1$) decreases the settling time and increases the percent overshoot of the transient particle trajectory

• We characterize the steady-state particle behavior:
  ▪ Increasing the ratio between the acoustic radiation force and the time-independent drag force ($K_1$) increases the oscillation amplitude around $x_s$
  ▪ The oscillation amplitude is dependent on the ratio between the time-dependent drag force and the particle inertia ($K_2$); and resonant values of $K_2$ increases the oscillation amplitude
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Ultrasound DSA in 1D: Problem statement

- **Critical problem**: Control the steady-state position of the particle by adjusting the ultrasound transducer parameters (amplitude and phase) to displace the ultrasound wave field node.
- Existing techniques require reflected ultrasound waves to be removed.

- **Objective**: Derive a method for unconstrained particle manipulation in 1D via phase control of two ultrasound transducers, taking all reflections into account.

Ultrasound DSA in 1D: Theoretical model

- **1D ultrasound wave field:**
  \[
  \frac{\partial^2 p}{\partial x^2} - k^2 p = 0
  \]

- **Boundary conditions:**
  \[
  n_j \cdot \nabla p = i \rho_f \omega v_j, \quad j \in \{1, 2\}
  \]

- **Ultrasound transducer parameters:**
  \[
  v_1 = A_1 e^{i \psi_1} \text{ at } x=0, \quad \text{and} \quad v_2 = A_2 e^{i \psi_2} \text{ at } x=L
  \]

- **Ultrasound wave field solution:**
  \[
  \Re [p(x)] = \frac{\rho_f}{2k \sin kL} \left( A_1 \cos \psi_1 \cos (k(L-x)) - A_2 \cos \psi_2 \cos kx \right)
  \]

- **Node location:**
  \[
  x(\psi_1, \psi_2) = \tan^{-1} \left( \frac{A_2 \cos \psi_2 - A_1 \cos \psi_1 \cos kL}{A_2 \cos \psi_1 \sin kL} \right) + \frac{mk}{\pi}, \quad m \in \mathbb{Z}
  \]
Ultrasound DSA in 1D: Simulated particle manipulation

- Particle manipulation achieved by applying a sequence of ultrasound transducer phases

Nodal location versus phase

Example particle trajectories

Pressure amplitude versus phase
Ultrasound DSA in 1D: Experimental particle manipulation

- Manipulate 350 μm diameter polystyrene sphere in a water reservoir

**Experimental setup**

**Desired particle trajectory**

**Theoretical and experimental particle displacement**
Ultrasound DSA in 1D: Conclusion

• We derive and experimentally validate a method for manipulating particles in 1D via independent phase adjustment of two ultrasound transducers.

• In contrast with existing techniques, the new technique accounts for all ultrasound reflections.

• We demonstrate continuous particle manipulation over multiple wavelengths $\Delta x = 2\lambda$. 
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Ultrasound DSA in 2D: Problem statement

- **Critical problem:** Relate ultrasound transducer parameters to the pattern of particles by formulating either a **forward** or **inverse problem**

\[
v = \begin{bmatrix}
v_1 \\
\vdots \\
v_N
\end{bmatrix}
\]

**Forward problem**

**Inverse problem**

- **Current techniques** for formulating the **inverse problem** are limited to:
  - Indirect solution methods
  - Specific reservoir geometries and ultrasound transducer arrangements
  - Specific patterns of particles

- **Objective:** Demonstrate a direct solution method for the **inverse problem** to enable creating a 2D user-specified pattern of particles in a reservoir with arbitrary geometry and ultrasound transducer arrangement
Ultrasound DSA in 2D: Boundary element model

- Relate the ultrasound transducer parameters to the ultrasound wave field using the boundary element method

**Boundary element model of the reservoir**

**Green’s 3rd identity**

\[
p(x) = \oint_S p(q) \frac{\partial G(q, x)}{\partial n(q)} - G(q, x) \frac{\partial p}{\partial n}(q) \, dS_q
\]

**Impedance boundary condition**

\[
\frac{1}{\rho_f c_f} \frac{\partial p}{\partial n} + ik \frac{p + kv}{Z_t} = 0
\]

- \( p \): Pressure
- \( G \): Green’s function
- \( K \): Ultrasound wave number
- \( \rho_f \): Fluid medium density
- \( c_f \): Fluid medium sound speed
- \( Z_t \): Transducer acoustic impedance
- \( v \): Ultrasound transducer parameter
Ultrasound DSA in 2D: Forward and inverse problems

- Solve the **forward problem** using boundary element method and acoustic radiation force theory to express the acoustic radiation potential as a function of the ultrasound transducer parameters

  \[
  \mathbf{v} = \begin{bmatrix} v_1 \\ \vdots \\ v_N \end{bmatrix}
  \]

  Ultrasound transducer parameters

  \[
  \mathbf{p}(x,y;\mathbf{v})
  \]

  Ultrasound wave field

  \[
  U(x,y;\mathbf{v})
  \]

  Acoustic radiation potential

  Boundary element method

  Acoustic radiation force theory

- Solve the **inverse problem** using constrained optimization

  User-specified pattern of nanoparticles

  Solve the optimization problem:

  \[
  \mathbf{v}^* = \arg\min_{\mathbf{v}} \frac{1}{N} \sum_{i=1}^{N} U(x_i, y_i; \mathbf{v})
  \]

  subject to \( |\mathbf{v}| = \alpha \)

  Required ultrasound transducer parameters
Ultrasound DSA in 2D: Validation procedure

1. Prescribe user-specified patterns
2. Solve the inverse problem
3. Apply ultrasound transducer parameters calculated from the inverse solution to the experimental or simulated reservoir

\[ v^* = \begin{bmatrix} v_1 \\ \vdots \\ v_N \end{bmatrix} \]
Ultrasound DSA in 2D: Experimentally obtained patterns

- Compare experimentally obtained patterns to prescribed patterns

4 ultrasound transducers

- The technique produces good agreement between prescribed and experimental patterns of particles
Ultrasound DSA in 2D: Simulated patterns

- Compare simulated patterns to prescribed patterns
- Increasing the number of ultrasound transducers enables creating more complex patterns of nanoparticles
- The technique is limited to features without sharp corners, and may result in additional pattern features, not prescribed by the user
Ultrasound DSA in 2D: Conclusion

• We introduce a direct solution technique for the inverse ultrasound directed self-assembly problem, which enables creating 2D user-specified patterns of particles in a reservoir with arbitrary geometry and ultrasound transducer arrangement.

• We validate the technique by comparing user-specified patterns to those created in simulated and experimental reservoirs.

• The technique enables using ultrasound DSA for:
  ▪ Biomedical devices
  ▪ Process control
  ▪ Manufacturing of engineered materials with unique physical properties
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Ultrasound DSA with SLA: Problem statement

- **Critical problem:** How to use ultrasound DSA to organize macroscale user-specified patterns of particles within a 3D printed engineered material
- Organize pattern of particles in liquid photopolymer resin, then fixate them in place via photo-curing

- **Objective:** Integrate ultrasound DSA with a bottom-up stereolithography (SLA) process based on a Digital Light Processing (DLP) projector to enable fabricating 3D engineered materials with user-specified microstructure

*Existing techniques:*
- Restricted to 2D materials
- Laser curing process disrupts the pattern of particles

Integrate ultrasound DSA reservoir lined with ultrasound transducers into existing SLA device (mUVe 1.1 DLP)

Ultrasound DSA with SLA: Manufacturing apparatus

- Stereolithography apparatus
- Signal generator
- Radio frequency amplifier
- Build plate
- Liquid resin
- Reservoir lined with ultrasound transducers
- Projector
3D print engineered materials containing user-specified patterns of particles via a three-step process.

**Step 1: Organize and fixate pattern of particles in place**
- Ultrasound transducers
- Reservoir
- Projector

**Step 2: Adhere cured resin layer to a build plate**
- Standing ultrasound wave
- Pattern of particles

**Step 3: Lift build plate and resin layer from reservoir**
- Liquid resin
- Cured resin layer

\[ \frac{\lambda}{2} \]

\[ h_0 \]

\[ h_f \]
Ultrasound DSA with SLA: Single-layer materials (1)

- Single-layer material specimens containing line patterns of nickel-coated carbon fibers

\[ \theta_d = 0^\circ \quad \theta_d = 45^\circ \quad \theta_d = 90^\circ \quad \theta_d = -45^\circ \]

- Pattern alignment quantification: fast Fourier transform (FFT) anisotropy

- Pattern alignment results
Ultrasound DSA with SLA: Single-layer materials (2)

- Single-layer material specimens with complex user-specified patterns of nickel-coated carbon fibers fabricated in multiple sections

Active ultrasound transducers and projector images for each material section (octagonal specimen)

Material specimens
Ultrasound DSA with SLA: Multi-layer materials

- Multi-layer material specimens containing Bouligand microstructure of nickel-coated carbon fibers
Ultrasound DSA with SLA: Functional materials

- Electrical conductivity measurement

Two-microprobe setup

“Wire resistance” $R_w$

“Insulator resistance” $R_i$

Current-voltage response

<table>
<thead>
<tr>
<th>$I$ [mA]</th>
<th>$V$ [V]</th>
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<tbody>
<tr>
<td>-100</td>
<td>-10</td>
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Conductive material specimen

1 mm

Resistance measurements

$\text{Log}_{10}(R [\Omega])$

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<tr>
<th>Line index</th>
<th>$R_i$</th>
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Ultrasound DSA with SLA: Conclusion

• We describe a manufacturing process for 3D printing engineered materials with arbitrary 3D macroscale geometry and user-specified microstructure

• Demonstrate the manufacturing process by fabricating:
  ▪ Single-layer materials containing user-specified patterns of particles
  ▪ Multi-layer materials containing a Bouligand microstructure
  ▪ Materials containing electrically conductive lines of nickel-coated carbon fibers

• Manufacturing process finds application in:
  ▪ Manufacturing of multifunctional composite materials
  ▪ Manufacturing of metamaterials with unique physical properties
  ▪ 3D printing materials with embedded insulated electrical wiring
Acknowledgements

- We acknowledge support from
  - Army Research Office contract W911NF-14-1-0565
  - NASA Grant NNX15AP30H
Achievements

• **Journal publications**
  - L. Homel, J. Greenhall, B. Raeymaekers, “Fabricating polymer nanocomposite materials with ultra-high weight fraction of carbon nanotubes using ultrasound directed self-assembly”, *under review*

• **Conference presentations**

• **Awards**
  - 2014 National Science Foundation Graduate Research Fellowship “Honorable Mention”
  - 2015 NASA Space Technology Research Fellowship Recipient
Questions