Supporting information

Light Induced Surface Tension Gradients for Hierarchical Assembly of Particles from Liquid Metals

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Sec. I: Physics setting for the particle trajectory simulation

The steady-state Marangoni flow pattern in liquid gallium induced by the Laguerre-Gaussian laser mode was simulated by coupling the laminar flow, the heat transfer in the fluid and the electromagnetic wave using a finite element method solver COMSOL Multiphysics®. The size of liquid gallium was 1000 μm in diameter and 50 μm in height. To guarantee the accuracy of the simulation results, an extremely fine and symmetric mesh containing 173,888 triangle elements was built. The solved results (e.g., electric field profile, temperature profile, etc.) stabilized as the mesh element number is greater than 145,800. (Figure S6)

The particle trajectory was simulated based on Newton’s second law:

$$\frac{d(m_p\vec{u})}{dt} = \vec{F}_D + \vec{F}_B + \vec{F}_G + \vec{F}_{Bouyant}$$  \hspace{1cm} (1)

where $\vec{F}_D$ is the drag force from the fluid flow, $\vec{F}_B$ is the Brownian force, $\vec{F}_G$ is the gravitational force, and $\vec{F}_{Bouyant}$ is the buoyant force. Here, the drag force from the fluid flow ($\vec{F}_D$) is given by:

$$\vec{F}_D = \frac{m_p(\vec{u} - \vec{v})}{\tau_p}$$  \hspace{1cm} (2)

where $\vec{u}$ is the velocity of particle, $\vec{v}$ is the velocity of fluid flow, and $\tau_p$ is the characteristic time for the particle. The amplitude of the Brownian force ($\vec{F}_B$) is given by:

$$\vec{F}_B = \zeta \sqrt{\frac{6\pi k_B \mu T d_p}{\tau_p}}$$  \hspace{1cm} (3)

where $k_B$ is the Boltzmann constant and $\zeta$ is a vector of independent, normally distributed random numbers with zero mean and unit standard variation as indicated in COMSOL. For the sticking probability of the particles at the liquid-solid interface was set to 50% (bottom side of liquid gallium). When particle stick on the boundary:

$$\vec{u} = 0$$  \hspace{1cm} (4)

otherwise, the particle would bounce elastically back into the fluid:

$$\vec{u} = \vec{u}_c - 2(\vec{n} \cdot \vec{u}_c)\vec{n}$$  \hspace{1cm} (5)

where $\vec{u}_c$ is the particle velocity when the particle approaches the boundary of the liquid gallium domain. At all other boundaries of liquid gallium, the particles would bounce back elastically.

Sec. II: Mean-squared displacement for the particle trajectory

The mean-squared displacement ($MSD(\tau_p)$) for the particle trajectory is
given by:

\[ \text{MSD}(t_p) = \langle [\vec{r}(t + t_p) - \vec{r}(t)]^2 \rangle \]  

(6)

where \( \vec{r} \) is the position of the particle at time \( t \) and \( t_p \) is the time step for the simulation. For all the datasets presented in Figure 2 of the main text, the time step was set as the characteristic time of the particle, i.e., for 20 \( \mu m \) tungsten particles, \( t_p \) was \( 6.72 \times 10^{-4} \) s.

**Sec. III: Entropy calculation of the particle assemblies**

In all results, the number of particles that were released into liquid gallium was 2000. We then used entropy to quantify the degree of order of the particle pattern assembly at the liquid-solid interface. To calculate the entropy for different particle assemblies, we equally divide the particle pattern into \( (\frac{1000}{n})^2 \) square lattices (i.e., “bin”) of size \( n \) and counted the number of particles in each bin. Here, the entropy for the patterns is defined as:

\[ S = -\sum_{i=1}^{(\frac{1000}{n})^2} \frac{N_i}{2000} \ln \frac{N_i}{2000} \]  

(7)

where \( N_i \) is the number of particles in the \( i^{th} \) bin.

To test the reproducibility of our calculations, we repeated each simulation 10 times and compared the entropy for the particle assembly obtained in different runs. A series of bin sizes were utilized for entropy calculation to avoid the impact of the bin size on the entropy results. As shown in Figure S7, no matter the size of the bin utilized, the relative entropy difference was less than 0.8% and the mean squared error was less than 0.6%, supporting the reproducibility of our calculations.

In addition, to quantify the enhancement of the degree of the order, we set the entropy for a completely random particle assembly composed of 2000 tungsten particles as the reference value \( S_{\text{ref}} \). In a completely random particle assembly, the possibility for a particle to assemble at different positions is the same. Therefore, with a 50 \( \mu m \) bin size, the entropy for a completely random particle assembly is given by:

\[ S_{\text{ref}} = -\sum_{i=1}^{400} \frac{5}{2000} \ln \frac{5}{2000} = 5.9915 \]  

(8)

Therefore, the reduction in entropy \( (\Delta S) \) is given by:

\[ \Delta S = \frac{S_{\text{ref}} - S_{\text{particle assembly}}}{S_{\text{ref}}} \]  

(9)

where \( S_{\text{particle assembly}} \) is the entropy for the specific particle assembly of interest. \( S_{\text{ref}} \) and \( S_{\text{particle assembly}} \) are calculated with the same bin size.
Sec. IV: Probability of particle-sidewall interaction

A particle can only interact with the sidewall when the distance between the particle and the sidewall is no more than the radius of the particle itself. Based on this assumption, the probability for the particle-sidewall interaction \((P_0)\) with different particle size can be given by:

\[
P_0 = \frac{\pi \left( d_f^2 - (d_f - d_p)^2 \right)}{\pi d_f^2} = \frac{2d_f d_p - d_p^2}{d_f^2}
\]

where \(d_f\) is the diameter of the liquid gallium (1000 \(\mu m\) in our model). The probability of the particle-sidewall interaction for 20 \(\mu m\) diameter particles is 3.96\%, while for 5 \(\mu m\) diameter particles, the probability drops down to 0.998\%. Therefore, as shown in Figure S1, for 5 \(\mu m\) diameter particles, less particles stick to the sidewalls (Figure S1B, sticking probability = unity), compared to the pattern produced from 20 \(\mu m\) diameter particles (Figure S1A, sticking probability = unity).

SUPPORTING TABLES

Table S1. Summary of elements that do not form compounds with liquid gallium stable above the energy hull cutoff \(^1\text{-}^7\)

|       |       |       |
|-------|-------|-------|
| H     | He    | Be    |
| B     | C     | Ne    |
| Al    | Si    | Ar    |
| Zn    | Ge    | Kr    |
| Cd    | In    | Sn    |
| Xe    | W     | Hg    |
| Tl    | Pb    | Bi    |

Table S2. Parameters for finite element model \(^8\text{-}^9\)

| Parameter | Physical Meaning                                      | Value                        |
|-----------|------------------------------------------------------|------------------------------|
| \(k_0\)   | Temperature coefficient of surface tension for liquid gallium | \(-6.6\times10^{-5} \text{ N/(m } \times \text{ K)}\) |
| \(C_p\)   | Heat capacity for liquid gallium                      | 381.072862 \text{ J/(kg } \times \text{ K)} |
| \(\rho\)  | Density of liquid gallium                            | 5592 \text{ kg/m}^3         |
| \(\rho_p\) | Density of tungsten particle                         | 1930 \text{ kg/m}^3         |
| \(k_T\)   | Thermal conductivity of liquid gallium               | 8.0844 \text{ W/(m } \times \text{ K)} |
| \(\alpha\) | Thermal expansion of liquid gallium                  | 3.0762                      |
| \(\mu\)   | Dynamic viscosity of liquid gallium                  | 0.64288 \text{ mPa } \times \text{ s} |

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| \( \sigma_f \) | Electric conductivity of liquid gallium | \( 7.1 \times 10^6 \text{ S/m} \) |
|-----|----------------------------------|-------------------|
| \( n \) | Real part of refractive index for liquid gallium at 645nm | \( n = 1.57434 + 6.38 \times 10^{-4} \) * \( (T - 273.15) \) |
| \( k \) | Imaginary part of refractive index for liquid gallium at 645nm | \( k = 7.48476 + 2.46 \times 10^{-3} \) * \( (T - 273.15) + 2.18 \times 10^{-6} (T - 273.15)^2 \) |
| \( \varepsilon \) | Emissivity of liquid gallium at 645 nm | \( \varepsilon = 0.0771 + 6.852 \times 10^{-5} \times T \) |

**SUPPORTING FIGURES**

![XY cross-section](image)

**Figure S1.** XY cross-section of the particle assembly with the sticking coefficient of the sidewalls set to unity (\( LG_{14} \) laser mode and \( w_0 = 125 \mu m \)). The diameter of the particles \( (d_p) \) are: (A) 20 \( \mu m \), and (B) 5 \( \mu m \), respectively. The sidewall is marked with solid black line and highlighted with a dashed black arrow. Scale bar for the particle pattern is 200 \( \mu m \).
Figure S2. Particle patterns under different maximum intensity value of the electric field ($E_{\text{max}}$) for particles with a diameter of 20 µm ($LG_{14}$ laser mode and $w_0 = 125$ µm). (A) $E_{\text{max}} = 3500$ V/m, (B) $E_{\text{max}} = 3700$ V/m, (C) $E_{\text{max}} = 3825$ V/m, and (D) $E_{\text{max}} = 4000$ V/m. Scale bar for the particle pattern is 200 µm.

Figure S3. Entropy of the particle pattern under different maximum intensity value of the electric field ($E_{\text{max}}$) calculated with different bin sizes ($LG_{14}$ laser mode and $w_0 = 125$ µm). The diameter of the particles ($d_p$) are: (A) 20 µm, and (B) 5 µm, respectively.
Figure S4. Particle patterns under different maximum intensity value of the electric field ($E_{\text{max}}$) for particles with a diameter of 5 $\mu$m ($LG_{14}$ laser mode and $w_0 = 125 \, \mu$m). (A) $E_{\text{max}} = 3500 \, V/m$, (B) $E_{\text{max}} = 2130 \, V/m$, (C) $E_{\text{max}} = 2350 \, V/m$, (D) $E_{\text{max}} = 2550 \, V/m$, (E) $E_{\text{max}} = 2790 \, V/m$, (F) $E_{\text{max}} = 2970 \, V/m$, (G) $E_{\text{max}} = 3400 \, V/m$, (H) $E_{\text{max}} = 3600 \, V/m$, and (I) $E_{\text{max}} = 4000 \, V/m$. Scale bar for the particle pattern is 200 $\mu$m.
Figure S5. Entropy of particle patterns under different $E_{\text{max}}$ values ($LG_{14}$ laser mode and $w_0 = 125 \mu m$) with drag coefficient from Schiller-Naumann model. The bin size for the calculation of entropy is 50 $\mu m$ for 20 $\mu m$ diameter particles (solid black line), and the bin size is 20 $\mu m$ for 5 $\mu m$ diameter particles (solid red line).

Figure S6. Impacts of mesh element number on the simulation result accuracy. Relative change of: (left y-axis, black circle) maximum value of electric field ($E_{\text{max}}$), (right y-axis, blue circle) maximum value of temperature in liquid gallium ($T_{\text{max}}$), (left y-axis, green circle) minimum value of temperature in liquid gallium ($T_{\text{min}}$).
Figure S7. Statistical analysis of the entropy calculations. Relative change of entropy (left y-axis, blue box) and mean squared error of entropy (right y-axis, black solid line) for the particle assembly obtained in 10 repeated runs.

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