Fixing Colloidal Motions at Water/Air Interface with Micrometer Scale Resolution

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ABSTRACT: Fast colloidal motions driven by surface tension gradient are created in a thin water layer. Unlike using solid boundaries to limit the colloidal flow, our work relaxes this condition by directly placing bulk fluid next to an open air environment. When the colloidal flow along the air/water interface is interfered with stationary objects, repetitive semicircular motions, that is, micro eddy, are frequently observed in domains as small as 2 μm. We assign the capillary convection between the liquid next to the air and that from the bulk as the driving force for the observed motions. Relationships among the maximum speed, temperature gradient, and thickness of the liquid layer are experimentally investigated and numerically analyzed. Our results could inspire future designs of micromechanical motors or fluidic mixing in a miniature device.

1. INTRODUCTION

Colloidal motions are of paramount importance to the diffusion in drug delivery,1−3 particle aggregation in material processing,4−6 and nutrients/waste exchange in cells.7,8 Their similarities to molecules and atoms, plus their easy-to-capture sizes and a relatively slow kinetics, further offer immense opportunities to the scientific community in revealing complex phenomena such as structure formation or crystallization.9−14 Largely, our understandings were gained via confining the colloids inside a closed-channel microfluidics. When a pressure difference between two ends of the channel is applied, fluid flows will trigger the motion of colloids.15,16 Whereas great successes have been achieved using these permanently fixed boundaries, closed-channel systems like implanting chips are inherently difficult to reconfigure, making minimal invasion challenging.17,18 Moreover, when substance exchange between two moving fluids is demanded, a complex device using solid boundaries presents little similarity to the above biological processes in vivo.19 To partially fill this gap, we report using surface tension gradient as an alternative to produce repetitive but also fast motions for colloids that are dispersed inside a channel-free system.

2. MATERIALS AND METHODS

Thin Liquid Layer. A liquid suspension of colloids is prepared by adding silica spheres into distilled water at a concentration of 2.0 wt %, followed by sonicating for 10 min. These monodispersed spheres are usually 2.6 μm in diameter, even though colloids with a diameter of 1.0 μm are also used when we need to measure the width of the air/water interface.

The resulting suspension is then dropped on a clean glass substrate, with another glass slide capping the top to confine the droplet and two spacers on the sides (See Figure 1). The glass slides we used are microscope cover glass (from Fisher Scientific) with a thickness of 200 μm. Because of the large gravity, the particles are all sitting on the bottom substrate and thus are on the same focal plane, with a relative ease in imaging and movie recording.

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Thermal Gradient. Two metallic wires are attached to the bottom glass slide and sit closely by the rim of the water droplet, with one serving as the heat source and another serving as the cold source. The combination of both then introduces a thermal gradient parallel to the glass slide. In our setup, the heat source is simply obtained by blowing the wire with a stream of hot air, along with a thermal couple on the surface of the welding spot to gauge the amount of heat needed. Usually, this is achieved by either tuning the electric voltage on the heat gun or attenuating the exposure time. Ice or dry ice crystals are used to trap the second wire to function as a cold source.

Characterization. The optical microscope used for imaging the thermocapillary flow is ML8000 Meiji equipped with a digital camera (Moticam 2000). This equipment enables us to record the movie of the colloidal motions, where the particle speed is extracted. Because observed particle flow is governed by the thermal gradient inside the liquid layer, different particle locations will have different motions. Our measurements are always performed at locations in the middle between the top position and the left position (shown in Figure 3a), where we expect an average thermal gradient.

3. RESULTS AND DISCUSSION

Surface tension is sensitive to temperatures, in which a spatial variation in temperature can induce nonuniform tensions or pressures. This uneven distribution over a liquid surface can further trigger tangential stress, resulting in fluid motion dubbed as thermocapillary convection or Maragoni flow.20−23 These convections have been applied to drive droplet-based microfluidic devices.24,25 Unlike conventional means of flow control using pressure26 or electricity,27 thermocapillary control operates without any mechanical moving parts. In return, those droplet-based systems have a smooth and continuous liquid surface, giving rise to random motions for the dispersed colloids. To fix colloidal motions in one direction, we use a thin liquid layer (see Figure 1) that originates from a controlled-drying technique previously developed for 2D colloidal crystallizations.9 To be noted, there are two unique features in this setup. First, two glass slides are used to confine the liquid, rather than an open-ended substrate with a large open surface of liquid.20−23 Hence, the convectional flow is confined in a plane parallel to the glass slides for clear observation. Second, the layer thickness is reduced to the micrometer scale, comparable to the size of the colloidal particles. This eliminates the effect of a buoyant force and gravity, minimizing particle motion in the normal direction to the glass slide.

Rotating colloids with some stationary ones serving as interfering bumpers along the air/water interfaces are shown in Figure 2a. (See movie 1 in the Supporting Information.) The moving trajectories of those rotating colloids imply the boundaries of the microeddies (highlighted with black dashed lines) and the rotation directions (labeled with arrows). Within these boundaries, either multiple particles or one single particle is detected in the action. For example, in the upper-left panel of Figure 2a, a large number of microparticles are rotating, with all of them redirected back by the bulk fluid. Another similar case is shown in the bottom-left panel. Whereas this one still involves multiple colloids, the collective motion has a smaller size. We suspect this difference is caused by the different distances between the interfering bumpers, which usually are defected particles sticking on the bottom glass. The distances between these particles also regulate the shapes of rotation to either axisymmetric or asymmetric. In brief, when the distance between the bumpers is large, the particle can gain a fast speed at the air/water interface before colliding with the bumper in the downstream. Because the collision has a tendency to lift the colloid over the bumper, a larger turning angle or longer distance away from the air/water interface will be resulted. Afterward, those redirected particle will follow the bulk fluid flow until it meets the bumper in the upstream. Because our observed flow at air/water interface is always faster (4 to 10 times) than that in the bulk fluid, this contrast easily redirects any slow moving particle back to the interface by manifesting as a small turning angle. Therefore, the trail in the bottom-left panel is asymmetric, but the top-left panel is otherwise. Frequently, when multiple particles are found lying closely next to each other at the interface (bottom-right panel), one can see the same features as the larger eddy exists in a bigger gap and all of the other ones follow an asymmetric pathway. Moreover,
these rotations are all in the same direction, different from conventional Marangoni flows,\textsuperscript{20–23} where adjacent eddies rotate opposite to each other.

To fully understand this motion, a micro eddy with only one particle rotating is detailed in Figure 2b, where five snapshots of the entire cycle with a time interval of 0.15 s in between are selected. (See movie 2 in the Supporting Information.) Schematic illustrations are placed beneath each frame for easy visualization (cover glass removed). In particular, one colloid moves slanted from left to right along a straight air/water interface first. At \( t = 0.45 \text{ s} \), this colloid was redirected to an opposite path and then completed one cycle of rotation after \( t = 0.6\text{ s} \). The entire trajectories of this repetitive rotation within 6 s are plotted in Figure 2c, with its speed variations mapped in the right panel. Peaks in the map suggest the colloid reaching a top speed of 200 \( \mu \text{m/s} \), followed by a sudden braking to a speed of zero in 0.2 s and then a quick acceleration to 50 \( \mu \text{m/s} \) (with an opposite direction) before going back to the linear motion. This half-elliptical rotation lasts more than 30 min (data not shown), implying that the microparticle is driven by a rather steady flow of water. One might argue that the colloid could be driven by an unsteady substrate or any unintentional vibrations, but our verdict is otherwise. If there is a short-lived vibration or movement involved, then a relative motion between the colloid and the water will exist. Resulting viscous force or friction from the liquid will then quickly dampen the colloidal motion and makes the rotation trajectories smaller and smaller. Whereas many of the trails in the left panel of Figure 2c are not identical, we cannot clearly see the dampening trend. Rather, the long-lasting events signaled a liquid vortex or eddy, with its features defining the motion of our colloids.

Now let us take a further look at the water layer and find the role of the air/water interface in the aforementioned colloidal rotations. We know that a thermal gradient inside the water droplet will generate uneven surface tensions,\textsuperscript{22} where the air/water interface at the cold zone has a larger surface tension and the air/water interface in the hot zone has a smaller one. This uneven surface tension can be treated as a surface shear stress (\( \tau \)).\textsuperscript{22} If we count the shape of the water droplet as a full dot (Figure 3a) and account for the temperature gradient for the surface tension, then we can derive the surface shear stress as \( \tau = \Delta \gamma_0 / 187 \pi \) (for details, see the Supporting Information), where \( \Delta T \) is the temperature gradient and \( \gamma_0 = 0.076 \text{ N/m} \) is the water surface tension at 0 °C.\textsuperscript{28} Physically, when this surface shear stress occurs inside a continuous water medium, the surface water will then move from the hot zone to the cold area and, to conserve the mass, a bulk liquid flow inside the surface medium will move with an opposite direction, as shown in Figure 3a. Because the surface shear stress exists only at the air/water rim, a very thin layer (or small mass) of water will join the circumferential motion, with its speed rapidly dropping to zero after a short depth \( (w) \) into the liquid (illustrated in the left panel of Figure 3b). Certainly, this matches well with what we observed in Figure 2, where only one colloid in depth is traveling along the interface with a linear motion, with multiple other ones drifting within the bulk water at a much slower speed and in an opposite direction. Now, if we place four particles at the water/air interface by splitting them with two on each side in the middle panel of Figure 3b, then flow streamlines of the water will be distorted.\textsuperscript{20} Namely, the quick interface flow from the bottom corner will bend inward to surpass the collision point. Among these bending streamlines, a few of them will even be redirected to follow the bulk flow. As such, we can clearly identify rotating flows with a closed loop between these two interfering blocks, manifested as a vortex or eddy. Whereas the interfering points guide the formation of bending, the temperature gradient is responsible for initiating the interface flow. Furthermore, we argue that these eddies have the same trajectories as those of rotating particles. (See the right panel.) Mostly, the colloids we used are on the micrometer scale, similar to that of the interface width; their motions at the interface are thus intrinsically sensitive to a slight interference at the air/water interface. Essentially, the original linear or circumferential motion of the colloid can be suddenly changed to an internal rotation at the interfering site, followed by a redirected flow to complete an eddy. As a consequence, minimum energy loss ensures the vortex or micro eddy is long-lasting.

To fully gauge the width of the air/water interface, colloidal motion speed, and their dependence on rate of temperature gradient, a fluid mechanics model\textsuperscript{29} with the following speed profile can be formulated (also shown in Figure 4a):

\[
v_x(x, y) = u(x) \left( 1 - \frac{y^2}{(h/2)^2} \right)
\]

In this profile, \( 1 - \left( \frac{y^2}{(h/2)^2} \right) \) represents a pressure-driven flow inside the \( x-z \) plane, and \( h \) is the thickness of the liquid layer, whereas \( u(x) \) denotes a flow portion driven by the surface shear stress on the \( x-z \) plane as (for details see the Supporting Information and Figure S1):

\[
u_x(x) = \frac{\Delta T \gamma_0}{187 \pi 
\frac{\mu_u}{\rho u} \left( 8 \pi e^{-\rho_0/4\rho u} - 1 + erf \left( \frac{-x}{2\sqrt{\mu_0/\rho}} \right) \right)
\]

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Substituting eq 3 back into eq 2, we have:

\[
\frac{y_0}{1.87\pi\mu\Delta T} \left( \frac{\mu\mu_0}{\pi\rho} \right)^{3/4} \rho_0^{1/4} = w \left[ 1 + \left( \frac{-w}{2\sqrt{\mu_0/\rho}} \right)^{3/2} \right] \]

The left side of eq 4 is a function of \( w \) and \( U_0/\Delta T \). (Note: \( t_0 \) is also proportional to the square of \( U_0/\Delta T \).) Hence, \( w \) is only dependent on \( U_0/\Delta T \); if \( \Delta T \) and \( U_0 \) are given, then \( w \) can then be informed.

To verify our model, the above three parameters (\( w, \Delta T \), and \( U_0 \)) are experimentally measured. Specifically, we used small colloids (diameter of 1.0 \( \mu m \)) as tags to measure the interface width (\( w \)) and plotted it as a function of water layer thickness (\( h \)), as shown in Figure 4a. To be noted, the interface width is dependent on the location, and we measured the parameter at locations near top-left corner of the liquid layer (see Figure 3a), where a medium value is expected. When the small colloids were used, we indeed found a clear boundary between the interface flow and the bulk one, where large clouds of colloids made the bulk flow a dark color. In contrast, the interface contains many fewer particles but all moving with a significant faster speed. The measured interface width spans from a few micrometers to more than 40 \( \mu m \), being linearly proportional to our predefined water layer thickness. Essentially, increasing the water layer thickness enlarged the air/water interface, which expanded the volume of the interface flow. When large colloids with a diameter of 2.6 \( \mu m \) are used to map the flow speed at this air/water interface, its dependence on both the rate of temperature gradient and the water layer thickness is obtained. In brief, when we kept the water layer thickness constant at 10 \( \mu m \), the colloidal motion was proportional to the rate of temperature gradient, with a maximum speed of 133 \( \mu m/s \) at a rate of temperature gradient of 620 °C/m (Figure 4b). To be noted, the measured speed is the colloidal speed (\( v_c \)), not the maximum speed (\( U_0 \)). When the colloid radius (\( r \)) is 1.3 \( \mu m \), the maximum speed (\( U_0 \)) of 290 \( \mu m/s \) is calculated using \( U_0 = v_c/(1 - ((h/2)^2 + r^2)/h^2)) = v_c(1 - ((h/2) + r^2)/h^2)). \) Therefore, with \( \Delta T \) (620 °C/m) and \( v_c \) (132 \( \mu m/s \)) known, eq 4 allowed us to calculate the air/water interface width (\( w \)) as 10.3 \( \mu m \), a value fairly close to our measurement (≈7 \( \mu m \)). When temperature gradient decreases to 200 °C/m, the interface width is still ~10.3 \( \mu m \), implying that \( w \) is relatively independent of temperatures. Because we know that \( w \) is a function of \( U_0/\Delta T \), the maximum speed then must be proportional to the rate of temperature gradient. Essentially, the previously mentioned colloidal speed of 200 \( \mu m/s \) is resulted at the temperature gradient of 900 °C/m.

### 4. CONCLUSIONS

In summary, fixed colloidal motions at the water/air interface are created with a micrometer scale resolution. Unlike conventional means of flow control using pressure or electricity, our colloidal motions are driven by surface tension gradient without any mechanical moving parts. Moreover, our work relaxes another condition of conventional microfluidics, where solid boundaries were essential. When stationary objects are blocking the air/water interface, micro eddies were frequently observed in domains as small as 2 \( \mu m \). We assign the capillary convection between the interface flow and the bulk one as the driving force for the observed motions. We found that the colloidal motion is linearly proportional to the thermal...
gradient, suggesting a good control in future designs of micromechanical motors or fluidic mixing in a miniature device.

ASSOCIATED CONTENT
3 Supporting Information
Surface shear stress, the mechanics modeling, and colloidal motion at the oil/water interface. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.

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