Assembly and manipulation of mesoscopic particles by active thermocapillary stress

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The temperature variation of the surface tension at a liquid-gas interface generates tangential thermocapillary stresses which produce flows in the ambient fluid. Here, we demonstrate that such active stresses can be produced in a controlled manner by inducing a microbubble in optical tweezers. An analytical solution of the thermocapillary problem, based on the Stokes and heat equations, yields the flow profile around the bubble. It is clear that under the action of the resulting flow, mesoscopic particles dispersed in the ambient fluid assemble in in rings at the bubble interface. We proceed to demonstrate this experimentally by inducing self-assembly of polystyrene microparticles on the bubble surface in rings. In addition, we show transport of a wide range of particles ranging from gold nanoparticles to polystyrene microspheres using thermophoretic motion of the bubble under translation of the optical tweezers. Most importantly, we are able to release particles captured on the bubble surface by modulating the bubble diameter controllably. We also study the flow fields around a pair of microbubbles theoretically and observe that these would allow for additional control on particle assembly and manipulation. We realize the theoretical predictions experimetally by growing two microbubbles adjacent to each other and modifying the trajectory of freely diffusing polystyrene microparticles which are in the vicinity of the bubbles. Our studies indicate that the active thermocapillary stresses induced by multiple microbubbles could offer routes to particle micromanipulation that would otherwise be difficult to achieve in optical tweezers.

I. INTRODUCTION

The study of active stress on mesoscopic particles in fluidic environments has evoked widespread scientific interest in recent times since it enables the understanding and ultimate control of fundamental processes involving fluid-particle interactions at a microscopic level, and leads to a variety of applications. The fundamental processes range from transport of organelles inside the fluidic environment in a cell [1], to the motion of cilia and flagella of swimming bacteria [2]. The analysis of the active stress involved in many such processes has led to the design of "active" particles [3], that often mimic natural microswimmers. These active particles move in pre-designed paths by interacting with their environment and exchanging energy by diverse processes including thermophoresis [4], electrophoresis [5], diffusiophoresis [6], etc. Such controlled motion of mesoscopic particles under different active stress has very significant implications in different areas including cell biology [7], nanomedicine [8], and micro-patterning [9]. Active stress can also be induced on microparticles in a fluid by manipulating the flow environment using different techniques of actuation [10] in microfluidic channels, and by generating surface stresses by controlled modulation of fluid-fluid or fluid-solid boundaries. The latter can be achieved by a number of processes such as electrowetting [11], thermocapillary action [12], and Marangoni stresses [13].

Recently, it has been show that the thermocapillary flow around a thermooptically generated bubble can be used to trap silica particles and nanotubes. These bubbles are generated by focusing the trapping laser on an absorbing substrate on the wall of a water filled trapping chamber. The rapid heating causes the water in the vicinity of the laser "hot spot" to spinodally decompose and grow into a bubble. The bubble reaches a steady state size determined by the laser power and remains thermophoretically trapped in the region of the temperature maximum. Since there is an appreciable temperature difference between the pole of the bubble which is in direct contact with the hot spot and its opposite pole which is farthest from the hot spot, an active Marangoni stress is immediately developed on the bubble surface. This active stress drives fluid flow towards the bubble and away from the wall. Particles are drawn towards the bubble due to this convective flow and attach to the bubble surface [14,15,18]. The hot spot can be translated and the bubble, driven by the strong thermophoretic forces, follows it. This provides a method for transporting particles that are attached to the bubble surface.

Such thermophoretic trapping mechanisms have several advantages of over standard optical tweezers. First, thermophoretic traps are agnostic to the dielectric constrast between the particle and the suspending medium. Thus, particles with negative dielectric constrast that are impossible to trap using standard optical means can easily be trapped thermophoretically. Second, thermophoretic traps can apply nN forces while optical traps can only apply much weaker forces in the range of a few hundred pN. Third, thermophoretic traps can transport multiple particles over large distances stably and

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simultaneously. While such trapping and manipulation by attaching particles to the bubble surface has been experimentally demonstrated, a controllable and consistent method for detaching the particles from the bubble surface without destroying the bubble is yet to be shown. This renders this otherwise robust particle transportation technique somewhat incomplete. Further, a clear picture of the active stress driven hydrodynamic flow is lacking. In this paper, we address both these issues. By solving the Navier Stokes and heat equations, we calculate the exact flow pattern of liquid around a laser induced microbubble. We go on to show how the flow pattern may be modified by having two bubbles adjacent to each other, and the implications on particle motion. Experimentally, we demonstrate interesting and reproducible self assembly of polystyrene beads of different sizes on the bubble surface - a phenomenon that is easily explained by our theoretical simulations. We also develop a technique for controllable release and attachment of particles to a bubble by modulating the bubble size, and proceed to demonstrate capture, transport, and release of gold and silver nanoparticles using a single microbubble. Finally, we provide a glimpse of the fascinating possibilities of manipulating the trajectories of micro-particles by trapping two micro-bubbles adjacent to each other, and observing particle trajectories in their vicinity. We believe that with proper choice of micro-bubble sizes and separations, this method can be eventually used as a tunable particle sorter - having the capability of sorting particles of different sizes continuously, since the bubble sizes and separations can be continuously tuned.

II. THEORY

We describe the system with a set of equations assuming a steady state, which are:

1. The Navier-Stokes equation describes the velocity of the fluid flow in the system:

$$\nabla P + \eta \nabla^2 v = 0 \tag{1}$$

2. Incompressibility condition:

$$\nabla . v = 0 \tag{2}$$

3. Heat equation:

$$\nabla^2 T = 0 \tag{3}$$

Here v, P, and T are the fluid velocity, pressure and temperature respectively. These set of equations have to solved together with a set of boundary conditions. These are:

1. $v = 0$ on the wall.
2. T = Room temperature at wall.
3. $v \to 0$ at $x = \infty$.
4. $p \to$constant at $x = \infty$.
5. ∇T is along z at $x = \infty$.

There are another set of boundary conditions on the bubble wall that balances stresses:

1. $v.n = 0$ on the surface of the bubble (no flow into the bubble).
2. $n.\nabla T = 0$ on the bubble surface (temperature gradient is only tangential).
3. Tangential stress = Normal temperature gradient (Marangoni condition).

III. EXPERIMENTAL RESULTS

The thermo-optic tweezers setup is based on an inverted Zeiss Axiovert.A1 microscope with a 100x 1.41 NA lens objective lens focusing the tweezers laser beam at 1064 nm into the sample chamber containing an aqueous dispersion of the sample (usually polystyrene microspheres of different diameters). We use two types of absorptive surfaces in the sample chamber: 1. A surface that is pre-coated by linear trails of a Mb-based soft oxometalate (SOM) material by a method developed by us (see Ref. [19]). The SOM material has finite absorption at 1064 nm, so that a hot spot is formed leading to a bubble when the tweezers laser is focused on any region along the trail. 2. A gold coated surface. We typically make abrasions on the gold coating with a sharp knife edge in order to create irregularities on the surface that can act as nucleation centers for bubble growth. The laser creates a hot spot due to enhanced absorption resulting from local plasmonic excitation, as a result of which the water gets heated above the boiling point to create a bubble. The absorptive surface (typically a microscope slide which forms the top surface of the chamber) is attached to a cover slip (bottom surface) by sticky tape. In both cases, the temperature of the hot spot would vary between around 373K (the threshold for bubble formation) to 644K - the latter corresponding to the critical temperature for water after which it cannot exist as a liquid with the surface tension tending to zero. The temperature of the hot spot can be modified by changing the laser intensity incident on it, which we typically achieve by changing the laser power.

A. Self assembly of particles on bubbles:

Once the bubble is formed, convective flows set in which draw particles towards it. As shown in the simulation results in Fig. 1, the flow lines tend to converge

along an equatorial circle of the bubble, so that we have an assembly of particles near that region. This is shown in Fig. 2, where we have a bubble of around 10 μmin diameter formed along a SOM trail in a sample chamber of the first type. 3 μm diameter polystyrene beads in aqueous dispersion follow the flow lines and assemble with time as shown in Fig. 2a - d. Video 1 in the multimedia files of the Supplementary Information shows the entire process in real time. We observe self assembly of a variety of particles including polystyrene beads of diameter 1, 3, and 10 μm (Video 2), as well as other particles including streptavidin coated magnetic beads of diameter 3 μm (Video 3), and gold (Video 4) and silver nanoparticles (Video 5) of around 10-100 nm in size. Note that the latter are notoriously difficult to trap using conventional optical tweezers due to their large scattering cross-sections. However, using this technique the scattering is rendered irrelevant since the particles are not exposed to light at all.

figures/Figure2.pdf

Figure 2. Time lapse images of 3 μm diameter polystyrene beads in aqueous dispersion assembling on a bubble of diameter around 10 μm grown on a SOM trail. The beads follow flow lines and assemble along an equatorial circle around the bubble. We see around 2 beads in panel a which is at t=0.5 s, while around 14 beads are distinctly visible in d, which is at t=13 s. These have been extracted from Video 1 in the multimedia files of the Supplementary Information.

B. Translation of bubbles with particles loaded

We are able to transport the particles thus assembled on the bubble as is shown in Videos 2-5 in the Supplementary Information. These include polystyrene beads, magnetic beads and nanoparticles as described in the earlier sections. The bubble is moved by translating the laser along the absorptive surface (of both types as described in Sec.III) on which the bubble is initially formed. The translation of the laser translates the hot spot as a result of which the Marangoni flows push the bubble in the direction of the higher temperature. We are able to translate bubbles with particles loaded on their surface with velocities of the order of 5 mm/s. Note that the translation of the polystyrene beads were performed on a SOM trail, while the gold and silver nanoparticles were moved along a gold surface.

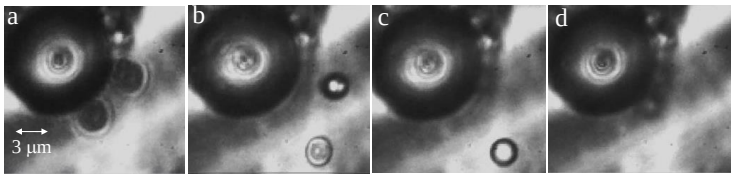

Figure 3. Time lapsed images of particle release and recapture by modulation of the bubble size. The particles are 3 μm diameter polystyrene beads. a) Two beads attached to the surface. b) Both have been released by changing the bubble size (see Video 6 in Supplementary Information). The bead at the bottom right corner is at a different z-depth compared to the bead closer to the bubble, so that they appear to be of different sizes since the focusing is different. c) The bead nearer to the bubble is back to the bubble surface (seen as a blur due at the side of the bubble due to different z-depth again), while the one farther away is still free. 4) The bead farther has been recaptured by the bubble (seen as a blur at the side once more).

C. Particle capture and release

Translation of bubbles with particles loaded on the surface has been demonstrated recently in Refs. [14,15]. Generally, particle release is performed by switching off the laser so that the bubble gradually collapses. However, we demonstrate a method of particle release without destroying the bubble, as is shown in Fig. 3. Here, we actually modulate the laser intensity by applying a square pulse to the laser current driver so that the power output of the laser changes according to the pulse amplitude. This causes the bubble diameter to change in sync with the laser power. Now, when the bubble diameter reduces so as to increase the radius of curvature of the bubble, the concomitant increase in surface energy is reduced by expelling the particles in contact with the bubble. Thus, the additional surface area due to the particles attached to the bubble is also reduced so that the energy is indeed minimized. Figure 3 shows time lapsed images of 3 μm diameter polystyrene beads being released and recaptured by the bubble due to the modulation of the bubble size. As the bubble diameter is reduced to a certain critical size, the particles are released, only to be recaptured once the bubble is back to the initial size. It is expected that larger particles would require a smaller bubble size to be released since they have larger surface area with a higher sticking force on the bubble surface.

D. Particle manipulation using two bubbles

In these set of experiments, we created two adjacent bubbles on neighbouring pre-existing SOM trails. The bubbles are shown in Fig. 4, of size around 24 and 28 μm respectively. The flow pattern around the bubbles are demonstrated in the simulation shown in Fig. 1b. To verify this flow pattern we have particles of diameter 3

μm in the aqueous dispersion, and their trajectories are highlighted in Fig. 4. It is clear that a separatrix can be identified between the two bubbles, and particles would be drawn towards a bubble depending on whether its trajectory lies above or below the separatrix. The position of the separatrix is modified with the change in size of the bubbles, as is apparent from simulations as shown in Fig. 1b. We can thus envisage the use of this technique to generally sort particles by size modulation of the two bubbles, where the position of the separatrix would be continuously modulated by changing the laser power, so that by a suitable choice of separation between the bubbles and modulation frequency, one can allow particles of a certain diameter to pass between the bubbles while others would be trapped on the bubble surfaces. We are currently working on some of these experiments.

IV. CONCLUSIONS

Acknowledgments

Thank you so much!

[1] Author, "Title", Journal **Volume**, page–numbers (year).