Long-Range Capture and Delivery of Water-Dispersed Nano-Objects by Microbubbles Generated on 3D Plasmonic Surfaces

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Supporting Information
Fig S.I. 1.1 Sketches of the optical setups for the white light and fluorescence images. The components are:
- Laser Ti:Sa; Coherent-Mira 900f
- Objectives: 60× Olympus LUCPLAN FLN; n.a.0.7 and 60× water immersion Olympus LUMPLFLN-W; n.a.=1
- White Led: MWWHL3 from Thorlabs
- Cube beam splitter non pol. 50/50 -- Zess fluorescence cube n°9
- Short pass filter: SPF650 from Thorlabs
- Camera CCD, Hamamatsu Orca R2
S.I. 2 Trapping of objects during the rapid expansion of the bubble

It is well known that colloidal particles and bacterial strains are inclined to be trapped at air-water interface.¹,² Interfacial accumulation of colloidal particles results from surface tension effects. In fact, as far as two liquids or fluids are immiscible, it is thermodynamically favorable for a particle to adsorb to the interface, no matter whether the particle is hydrophobic or hydrophilic (although hydrophobic interactions promote the accumulation).¹,² Once a particle has been located at an infinitely large interface, the energy gain is:

\[ \Delta E = -\pi r_p^2 \gamma_{wa} (\cos \theta - 1)^2 \]

Where \( r_p \) is the radius of particle, \( \gamma_{wa} \) the interfacial energy of water-air interface, \( \theta \) is the wetting angle of the particle. In the particular case of a micrometer sized expanding bubble, there are three forces at play, namely the component of surface tension force along the radius of the bubble, \( F_s \), Laplace pressure force from inside the bubble, \( F_p \), and drag force \( F_d \).

Figure S.I. 2.1: Sketch of the particle located at the bubble interface between air and water. Where \( r_p \) is the radius of particle, \( F_s \) is the component of surface tension force along the radius of the bubble, \( F_p \) represent the Laplace pressure force from inside the bubble and \( F_d \) the drag force.
At the equilibrium we have the condition $F_s + F_p + F_d = 0$. From Laplace pressure, it can be shown\(^3,4\) that
\[
F_p = \frac{2 \pi \gamma_{wa}}{R_B} (r_p \sin \alpha)^2,
\]
while
\[
F_s = 2 \pi \gamma_{wa} r_p \sin \alpha \sin(|\alpha - \theta|)
\]
with $R_B$ bubble radius and $\alpha$ the half angle between the particle’s center and particle-liquid-gas line of contact. The drag force $F_d$ due to rapid bubble expansion can be calculated from Stokes' law $F_d = 6 \pi \eta r_p v$ where $\eta$ is the viscosity of water, and $v$ is the relative velocity between the particle and the fluid. Considering values $r_p \approx 2 \cdot 10^{-7} \text{m}$, $v \approx 100 \mu\text{m/s}$ and $R_B \approx 10^{-5} \text{m}$ from our experiments, it results that $F_d \approx 4 \cdot 10^{-13} \text{N}$, significantly smaller than the Laplace pressure force $F_p \approx 1.8 \cdot 10^{-9} \text{N}$ and surface tension force $F_s$. Therefore the equilibrium is given by the condition:
\[
\frac{F_s}{F_p} = \frac{R_B \sin(|\alpha - \theta|)}{R \sin \alpha} = 1
\]
The Laplace pressure force $F_p$ pushes the particle out of the bubble and the surface tension force $F_s$ acts as a restoring force directed toward the center of the bubble bringing the particle back in equilibrium.

For a very large bubble radius $R_B$, when also the Laplace pressure can be neglected ($F_p = 0$), the radial component of surface force $F_s = 0$ and $\alpha = \theta$.

As explained above, the drag force $F_d$ cannot contribute to the detachment of particles, while it actually contributes to the accumulation. In fact in the case of a static interface, accumulation of particles is mainly a diffusion-limited process, depending on the particle arrival rate at interface. In the presence of a moving interface, as the case of a rapidly expanding bubble investigated in this manuscript, the particle arrival rate is strongly increased. The effectiveness in trapping particles increases with the bubble expansion velocity $v_f$ and particle radius $r_p$. 
Let’s now consider a bubble expanding at constant velocity $v_f$ with radius $R(t) = v_ft$ and a particle at position $r$ respect to the centre of the bubble (Figure S.I. 3.2), from the mass conservation law, the velocity field around the bubble decays as $r^{-2}$ and has the general form $u(r, t) = \left(\frac{R(t)}{r}\right)^2 v_f$. If we assume that the particle is subject only to Stokes forces $F = 6\pi\eta r_p(u(r, t) - \dot{r})$ with $\eta$ dynamic viscosity, $r_p$ and $\dot{r}$ particle radius and velocity, the equation of motion of the particle can be written as:

$$m \ddot{r} = 6\pi\eta r_p \left(\frac{R(t)}{r}\right)^2 v_f - \dot{r}$$

To evaluate the dynamics of particles in the proximity of expanding bubble, we can assume $r \approx R(t)$, and the equation simplifies to $\ddot{r} = a(v_f - \dot{r})$ where $a = \frac{6\pi\eta r_p}{m}$. The solution is:

$$r(t) \approx v_f t - \frac{v_f}{a} + r(0)$$

where $r(0)$ is the particle position at $t=0$. 

Figure S.I. 3.2: Sketch of the bubble expanding at constant velocity $v_f$ with radius $R(t)$ and a particle at position $r$ respect to the centre of the bubble.
For the rapidly expanding bubble to reach and trap the particle \( R(t) = v_f t > r(t) \), that leads to the simple relation \( r(0) < \frac{v_f}{a} = \frac{2v_f \rho r_0^2}{9\eta} = r_{\text{trap}} \). Particles below \( r_{\text{trap}} \) are reached and trapped, while above \( r_{\text{trap}} \) they are accelerated to \( v_f \).

### S.I. 3 Analytical simulation details

To simulate numerically the collapse of a gas bubble in liquid water and the fluid flows in vicinity of a micrometer sized structure, we use the classical equations of fluid dynamics coupled to the “level set method” for the dynamics of interface implemented in the “OpenFoam free CFD Software”. We perform two dimensional simulations assuming the liquid to be an incompressible Newtonian fluid and take into account instead of the compressibility of the gas in the bubble by regulating the bubble pressure in agreement to the ideal gas law, once fixed initial external pressure \( P_{\text{ext}} \), bubble pressure \( P_0 \) and volume \( V_0 \).

The initial bubble radius is \( r_0 = 3\mu m \), the antenna and deflecting wall are both \( 4\mu m \) high. We initially set the system at equilibrium with \( P_0 = \frac{\sigma}{r_0} + P_{\text{ext}} \) satisfying Laplace equation. The bubble collapse is obtained by increasing the external pressure \( P_{\text{ext}} \) through a step function. The equilibrium radius \( r(t) \) is then obtained from relation \( P_0 \frac{r_0^2}{r(t)^2} = \frac{\sigma}{r(t)} + P_{\text{ext}} \).

The water-air surface tension is taken as \( \sigma = 0.073N/m \) and the wetting angle of the fluid on the nanostructure is fixed to \( \theta = \pi/3 \).

To solve the model equations, the global computational domain has been meshed by 12000 elements approximately.
Figure S.I. 3.1: From left to right time laps of the bubble collapse as reconstruct by the 2D analytical simulation. The complete sequence can be seen in the video: SI_video4_AVI.

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