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Supporting information for

Direct observation of the attachment behavior of hydrophobic colloidal particles onto a bubble surface

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Velocity evolution in the case of a HMDS-modified bead

Figure S1 shows the velocity evolution of a HMDS-modified bead through an attachment event. The bead exhibited the jump-in behavior right after landing, and the maximum velocity was larger than $u^* = 1.0$. The increase in the velocity of HMDS-modified beads is smaller than that of TMCS-modified ones because the fluid resistance did not decrease largely owing to a small degree of the penetration into a bubble.

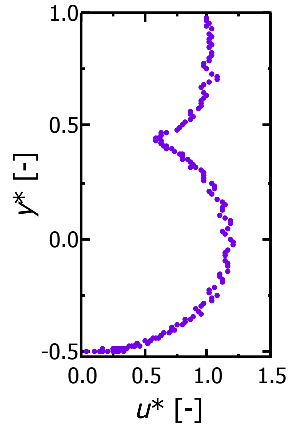

Figure S1. Velocity evolution of a HMDS-modified bead through an attachment event

Calculation procedure to obtain a static contact angle from a velocity of a particle

We assumed that the step-wise increase in a particle velocity was induced by the decrease in the fluid resistance due to the jump-in to satisfy the static contact angle of a particle surface (see Figure 6c). Based on this assumption, the static contact angle, θ [rad], was calculated from the maximum velocity, which is determined by the immersed part of the area of a particle in water. The projected area A_{pAir} $[\mathrm{m}^2]$ and volume V_{Air} $[\mathrm{m}^3]$ of the exposed potion of a single particle to the air are expressed as Equations (1) and (2). Those of the immersed portion of the particle in water, A_{pLiq} $[\mathrm{m}]$ and V_{Liq} $[\mathrm{m}^3]$, are given by subtracting A_{pAir} and V_{Air} from the whole surface area and volume as in Equations (3) and (4).

$$\begin{aligned} A_{\mathrm{pAir}} &= \frac{d_{\mathrm{p}}^2}{2}\int_0^{\theta}(1-\cos^2\alpha)d\alpha \\ &= \frac{d_{\mathrm{p}}^2}{8}(2\theta - \sin 2\theta) \end{aligned} \tag{1}$$

$$\begin{aligned} V_{\mathrm{Air}} &= \frac{\pi d_{\mathrm{p}}^3}{8}\int_0^{\theta}(1-\cos^2\alpha)\sin\alpha\, d\alpha \\ &= \frac{\pi d_{\mathrm{p}}^3}{8}\left(\frac{2}{3}+\frac{1}{3}\cos^3\theta - \cos\theta\right) \end{aligned} \tag{2}$$

$$A_{\mathrm{pLiq}} = \frac{\pi d_{\mathrm{p}}^2}{4} - A_{\mathrm{pAir}} \tag{3}$$

$$V_{\mathrm{Liq}} = \frac{\pi d_{\mathrm{p}}^3}{6} - V_{\mathrm{Air}} \tag{4}$$

Here, d_{p} [m] is the diameter of the particle, and α [rad] is the angle between a tangential line of a bead and air-water interface (see Fig 6c, where it is expressed as θ [rad]). Fluid resistance, F_{D} [N], is then expressed as a function of Re_{pAir} [−] and Re_{pLiq} [−], which are the Reynolds numbers in air and water respectively,[1,2] because both Reynolds numbers are smaller than 2, which is in the Stokes region.

$$
\begin{aligned}
F_D &= \frac{1}{2}\frac{24}{Re_{\mathrm{pAir}}}A_{\mathrm{pAir}}\rho_{\mathrm{Air}}u^2 + \frac{1}{2}\frac{24}{Re_{\mathrm{pLiq}}}A_{\mathrm{pLiq}}\rho_{\mathrm{Liq}}u^2 \\
&= \frac{1}{2}\frac{24\mu_{\mathrm{Air}}}{\rho_{\mathrm{Air}}d_{\mathrm{pAir}}u}A_{\mathrm{pAir}}\rho_{\mathrm{Air}}u^2 + \frac{1}{2}\frac{24\mu_{\mathrm{Liq}}}{\rho_{\mathrm{Liq}}d_{\mathrm{pLiq}}u}A_{\mathrm{pLiq}}\rho_{\mathrm{Liq}}u^2 \qquad (5)\\
&= \frac{12\,\mu_{\mathrm{Air}}A_{\mathrm{pAir}}}{d_{\mathrm{pAir}}}u + \frac{12\,\mu_{\mathrm{Liq}}A_{\mathrm{pLiq}}}{d_{\mathrm{pLiq}}}u
\end{aligned}
$$

$$d_{\mathrm{pAir}} = \sqrt{\frac{4A_{\mathrm{pAir}}}{\pi}} \qquad (6)$$

$$d_{\mathrm{pLiq}} = \sqrt{\frac{4A_{\mathrm{pLiq}}}{\pi}} \qquad (7)$$

Here, u [m/s] is the velocity of a bead. μ_{Air} [Pa · s] and μ_{Liq} [Pa · s] indicate the viscosity of air and water, respectively. ρ_{Air} [kg/m^3] and ρ_{Liq} [kg/m^3] are the density of air and liquid, respectively. The buoyancy force, F_{B} [N], is expressed by the following equation.

$$F_{\mathrm{B}} = \rho_{\mathrm{Air}}V_{\mathrm{Air}}g + \rho_{\mathrm{Liq}}V_{\mathrm{Liq}}g \qquad (8)$$

In the events of the particle attachment, the inertia can be neglected due to small Reynolds numbers. The terminal velocity of the particle is determined by the balance between the fluid resistance and the external force acting on a particle as in Equation (9).

$$0 = \frac{\pi}{6}\rho_{\mathrm{p}}d_{\mathrm{p}}^3 \mathrm{g}\sin\phi \; - F_{\mathrm{D}} - F_{\mathrm{B}}\sin\phi \qquad (9)$$

Here, ρ_{P} [kg/m^3] is the density of a particle, and ϕ [rad] is the instantaneous angle between the vertical y-axis and the segment connecting the bubble center to the center of mass of the sliding particle. Because the viscosity and density of air are much smaller than those of water, the fluid resistance and buoyancy force of air can be neglected. Finally, we get the following formula.

$$u^*(\phi, \theta) = \sin\phi \left(1 + \frac{\sin 2\theta}{2\pi} - \frac{\theta}{\pi}\right)^{-\frac{1}{2}} \left(\frac{4S - (2 - \cos^3\theta + 3\cos\theta)}{4(S-1)}\right) \tag{10}$$

Here, $S = \rho_\mathrm{P}/\rho_\mathrm{Liq}$ is the bead-to-liquid density ratio. Equation (10) gives the relationship between the velocity u and the static contact angle θ of a particle. Hence, the static contact angle can be uniquely determined from the maximum velocity of a particle after the jump-in.

References

1 G. G. Stokes, *Trans. Cambridge Philos. Soc.*, 1850, **IX**, 8.

2 A. Haider and O. . Levenspiel, *Powder Technol.*, 1989, **58**, 63.