Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Directional Passive Transport of Nanodroplets on General Axisymmetric Surfaces

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Theory

Geometrical expressions for r_1, r_2, dR_c/ds, and H

Using the geometric relationship in Fig. 3, the following relations are obtained,

$$H = r_1 + r_1 \sin(\theta - 90°), \tag{S1}$$

$$o_d o_s = R + H - r_2, \tag{S2}$$

$$o_d o_s{}^2 = r_2^2 + R^2 - 2 r_2 R \cos\theta. \tag{S3}$$

r_1 can be directly obtained from Eq. (S1),

$$r_1 = \frac{H}{1 - \cos\theta}. \tag{S4}$$

Substituting Eq. (S2) into Eq. (S3) gives,

$$r_2 = \frac{H(H + 2R)}{2 \cdot (H + R(1 - \cos\theta))}. \tag{S5}$$

To determine the variation of R_c along the axisymmetric surface, we assume an infinitesimal virtual displacement, ds, (or correspondingly $d\alpha$) of the droplet and the resulted radius of curvature, $R_c^{'}$ can be computed by (Fig. S1),

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$$R_{\mathrm{c}}^{'} = l + \tan(\alpha_z + d\alpha) \cdot d\alpha \cdot l \,. \tag{S6}$$

l can be written as,

$$l = R_{\mathrm{c}} + \tan\alpha_z \cdot ds \,. \tag{S7}$$

Combining Eq. (S7) and the relation, $d\alpha = ds/R_s$, Eq. (S6) is converted to,

$$dR_{\mathrm{c}} = R_{\mathrm{c}}^{'} - R_{\mathrm{c}} = \tan\alpha_z ds + \tan(\alpha_z + d\alpha) \cdot \frac{R_{\mathrm{c}}}{R_{\mathrm{s}}} \cdot ds + \frac{\tan(\alpha_z + d\alpha) \cdot \tan\alpha_z}{R_{\mathrm{s}}} \cdot (ds)^2 \,. \tag{S8}$$

Since $\tan(\alpha_z + d\alpha) \approx \tan\alpha_z$, dividing both sides of Eq. (S8) by ds and eliminating the infinitesimal quantity, Eq. (S8) becomes,

$$\frac{dR_{\mathrm{c}}}{ds} = (1 + \frac{R_{\mathrm{c}}}{R_{\mathrm{s}}}) \tan\alpha_z \,. \tag{S9}$$

For a droplet with radius r_{d}, its volume is $V_{\mathrm{d}} = 4\pi r_{\mathrm{d}}^3/3$. For this droplet placed on axisymmetric surfaces, the height of the droplet, H can be approximated by that of the droplet rested on a flat surface with the same volume. If the contact radius of droplet on a flat surface is denoted as r_0, the volume of the droplet can be expressed as,[1]

$$V = \frac{\pi}{3} r_0^3 (1-\cos\theta)^2 (2+\cos\theta) = \frac{4\pi r_{\mathrm{d}}^3}{3} \,. \tag{S10}$$

H can be computed by,

$$H = r_0 (1-\cos\theta) = r_{\mathrm{d}} \sqrt[3]{\frac{4(1-\cos\theta)}{2+\cos\theta}} \,. \tag{S11}$$

Driving force for barrel shaped droplets

According to Eq. (1), by assuming H_{m} is a constant, Eq. (1) can be written as,

$$\frac{dP}{ds} = -\frac{2\gamma\tan\alpha}{(R + H_{\mathrm{m}})^2} \,. \tag{S12}$$

Thus, the driving force can be computed by,

$$F = -\frac{dP}{ds} \cdot V_{\mathrm{d}} = -\frac{2\gamma \tan\alpha}{(R + H_{\mathrm{m}})^2} \cdot \frac{4\pi r_{\mathrm{d}}^3}{3}. \tag{S13}$$

Work of adhesion

The MD system is modelled by a droplet resting on a cylinder, as shown in Fig. 3. The total surface free energy change (per unit area) in forming a droplet from the cylinder equilibrated with vapor is (Fig. S5),[2,3]

$$\Delta F_{\mathrm{SV}} = \frac{1}{A_{xz}} \left(A_{\mathrm{LV}} \cdot \gamma + A_{\mathrm{LS}} \cdot (\gamma_{\mathrm{SL}} - \gamma_{\mathrm{SV}}) \right), \tag{S14}$$

where A_{LV} represents the liquid-vapor interface area, A_{LS} is liquid-solid interface area, A_{xz} denote the project area of A_{LS} onto the (x, z) plane, γ_{SL} and γ_{SV} are the solid to liquid and solid to vapor surface tensions respectively. As displayed in Fig. 3(a), the shapes of A_{LS} and A_{xz} are both ellipses. Their surface areas equal to $A_{\mathrm{LS}} = \pi ab$ and $A_{xz} = \pi a' b'$, where a and a' denote the length of the semi-minor axis, b and b' are the length of the semi-major axis. As illustrated in Fig. 3(b), it is obtained that $a = R \cdot \phi$ and $a' = R \cdot \sin\phi$, where ϕ represent the tangent-chord angle and $R = R_{\mathrm{c}}$. Since $b = b'$, the area ratio of A_{LS} / A_{xz} (defined as λ) is equal to $\lambda = a/a' = \phi/\sin\phi$.

The work of adhesion is the work needed to separate the droplet and the solid surface perpendicularly from each other against the adhesive force between them.[3] It is required that the droplet separated from the surface does not change its shape. Under this condition, the total free energy of the constrained droplet (per unit area) as shown in Fig. S5 is,[3]

$$\Delta F_{\mathrm{V}} = \frac{1}{A_{xz}} \left(A_{\mathrm{LV}} \cdot \gamma + A_{\mathrm{LS}} \cdot \gamma \right). \tag{S15}$$

The work of adhesion is the free energy change (per unit area) from the initial state to the final state (Fig. S5),

$$w_{\mathrm{ad}} = \Delta F_{\mathrm{V}} - \Delta F_{\mathrm{SV}} = \lambda(\gamma - \gamma_{\mathrm{SL}} + \gamma_{\mathrm{SV}}) . \tag{S16}$$

According to the classical Young's equation,

$$\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} = \gamma \cdot \cos\theta . \tag{S17}$$

Plugging Eq. (S17) into Eq. (S16) gives,

$$w_{\mathrm{ad}} = \lambda\gamma(1+\cos\theta) . \tag{S18}$$

The form of Eq. (S18) is analogous to the modified Young-Duprè equation in Ref. 4-5, except that the coefficient λ is different. The tangent-chord angle ϕ can be determined from the geometric relationship shown in Fig. 3(b),

$$R_{\mathrm{c}} \sin\phi = r_2 \sin(\theta+\phi) = r_2(\sin\theta\cos\phi + \cos\theta\sin\phi) . \tag{S19}$$

For convenience, r_2 is approximated by $r_2 \approx r_{\mathrm{d}}$. Dividing both sides of Eq. (S19) by $\sin\phi$, ϕ can be expressed as,

$$\phi = \arctan\frac{\sin\theta}{R_{\mathrm{c}}/r_{\mathrm{d}} - \cos\theta} . \tag{S20}$$

Theoretical model for *f*

The retentive force due to contact angle hysteresis is given by,[6]

$$f = kr_{\mathrm{ca}}\gamma(\cos\theta_{\mathrm{r}} - \cos\theta_{\mathrm{a}}) , ds \tag{S21}$$

where *k* is a coefficient that depends on the shape of droplets, r_{ca} is the contact-area radius, θ_{r} and θ_{a} are receding and advancing contact angle respectively. Theoretically, the energy needed to move a droplet on the solid surface by a distance δ should overcome the work of adhesion,[4,5]

$$f\delta = w_{\mathrm{ad}}\delta\pi r_{\mathrm{ca}} . \tag{S22}$$

Plugging Eq. (S21) into Eq. (S22) yields,

$$\cos\theta_{\mathrm{r}} - \cos\theta_{\mathrm{a}} = \frac{\pi}{k}\lambda(1+\cos\theta) . \tag{S23}$$

Combining Eq. (S21) and Eq. (S23), f can be written as,

$$f = \lambda r_{\mathrm{ca}} \gamma (1 + \cos\theta) \pi \,. \tag{S24}$$

It is noted that r_{ca} is approximated by the contact radius of a droplet with the same volume placed on a flat surface,

$$r_{\mathrm{ca}} \approx r_0 \sin\theta = 4^{1/3} r_{\mathrm{d}} \sin\theta \left(1 - \cos\theta\right)^{-2/3} \cdot (2 + \cos\theta)^{-1/3} \,. \tag{S25}$$

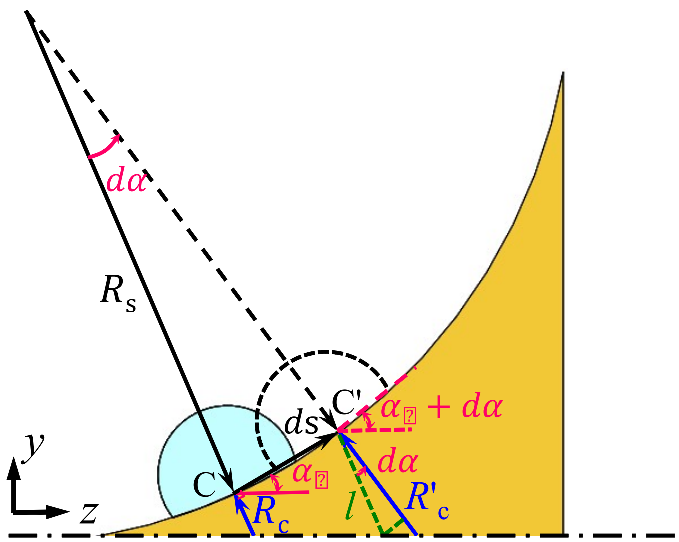

Fig. S1 Schematic illustration of a droplet with a virtual displacement *ds* on an axisymmetric surface

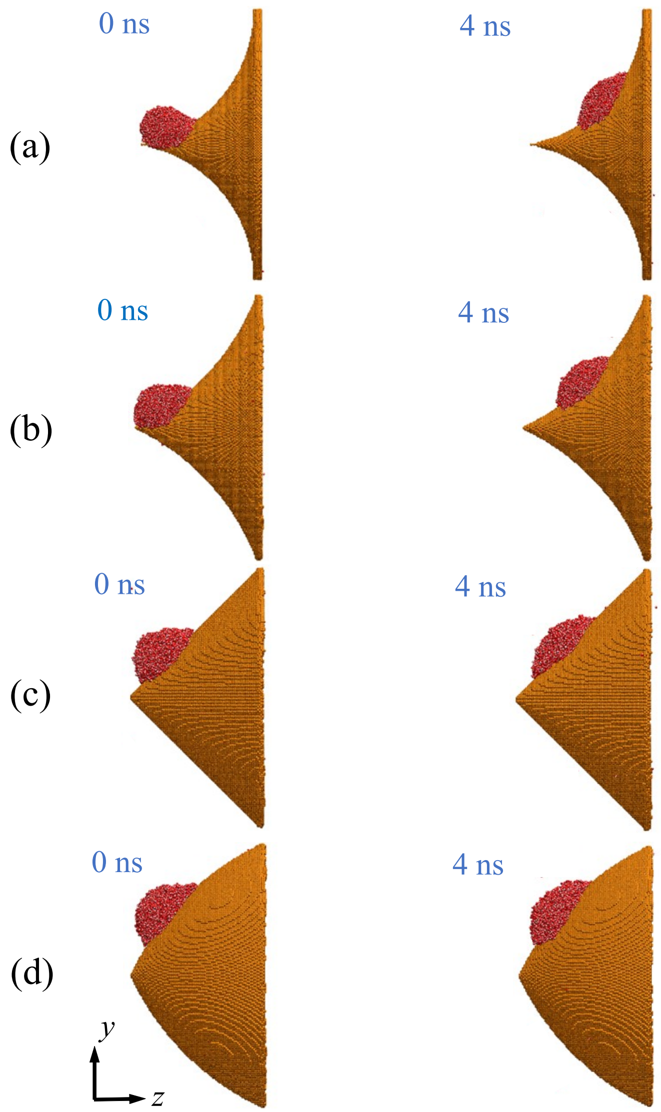

Fig. S2 Snapshots of MD simulation systems ($r_d = 3.5$ nm and $\varepsilon_{\text{ws}} = 200$ K) at the time $t = 0$ ns and $t = 4$ ns respectively for (a) α=10^o , (b) α=25^o , (c) α=45^o , (d) α=65^o .

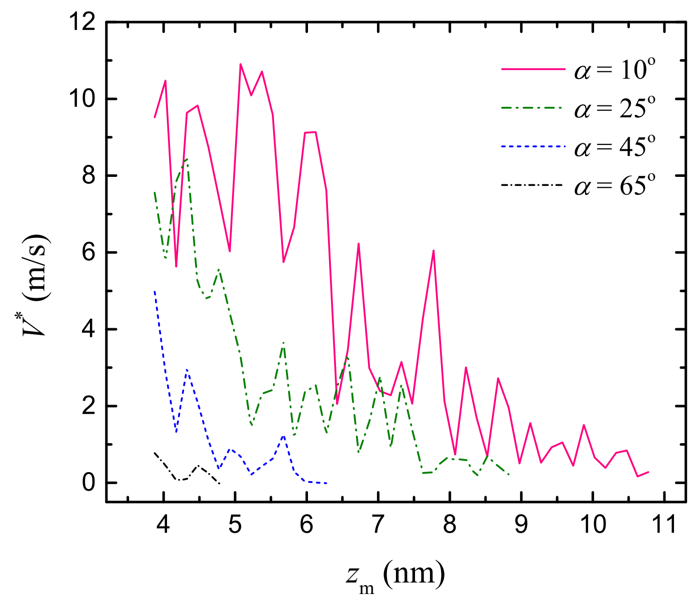

Fig. S3 Velocity of the droplet ($r_d = 3.5$ nm) versus z_m for various α with $\varepsilon_{ws} = 200$ K

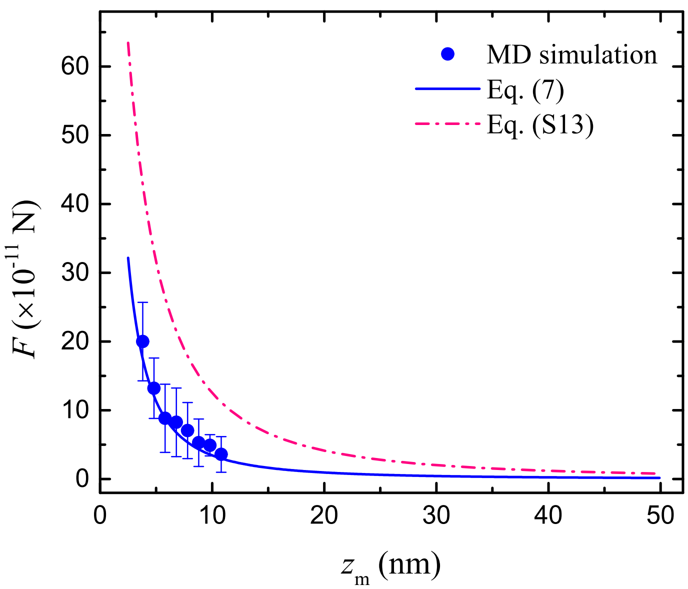

Fig. S4 Comparison of the predictions of the driving force of a droplet ($r_d = 3.5$ nm) on the conical surface with α=45^o and $\varepsilon_{\mathrm{ws}} = 200$ K using Eq. (7) and Eq. (S13).

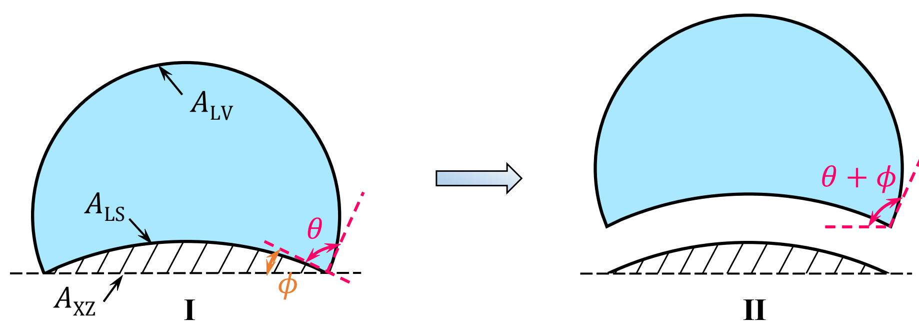

Fig. S5 The model for the free energy of adhesion

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