

Supplementary Materials
Generation of Motion of Drops with Interfacial Contact

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A. List of Symbols used in the Text

θ (°) : Angle of contact of the liquid drop with a substrate

ΔG (J) : Free energy of adhesion

γ_{lv} (N/m) : Surface tension of liquid in contact with air

γ_w (N/m) : Surface tension of water

R (m) : Radius of drop

F_Y (N) : Unbalanced Young's force experienced by the liquid drop

F_d (N) : Viscous Drag force

η (Pa.s) : Dynamic viscosity of liquid

V (m/s) : Velocity of liquid drop

Ca : Capillary Number

V^* ($\equiv \gamma / \mu$, m/s) : Capillary velocity of a liquid drop

R^* ($\equiv R(d \cos \theta / dx)$) : Non-dimensional value of radius of liquid drop obtained by multiplying drop radius with the gradient of the average contact angle [$\cos \theta = (\cos \theta_a + \cos \theta_r) / 2$].

P (Pa) : Laplace pressure within the liquid drop

ξ (m) : Local height of the drop

$\langle V \rangle$ (m/s) : Volumetric drop velocity

κ (m^{-1}) : Curvature (i.e. inverse of the radius of curvature) of liquid drop

$(\cos \theta_r - \cos \theta_a)$: Dynamic hysteresis of contact angle

k_s (N/m) : Spring constant of a liquid drop

R_o (m) : Equilibrium value of radius of liquid drop

R^\pm , R_a , R_r (m) : Maximum or minimum value of radius of drop corresponding to advancing (R_a) or receding (R_r) states.

u_o (J) : Energy barrier associated with the corrugated surface

λ (m) : Correlation length of the contact line pinning sites

\mathcal{L} (m): Larkin length

θ^\pm ($^\circ$) : Maximum or minimum value of contact angle of liquid drop with substrate corresponding to advancing (θ_a) or receding (θ_r) angles.

$$\phi = f(u_o / k_s \lambda^2)$$

$\zeta(\mathbf{r})$ (N/m): Friction factor

K (m^2/s^3) : Noise strength

$f(t)$ (m/s^2) : Random noise pulse or time varying acceleration

τ_c (s) : Duration of the noise pulse

x_1 : Position coordinate of the contact line of the drop

x_2 : Position coordinate of the bulk of the liquid drop

m (kg) : Mass of a liquid drop

ζ (kg/s) : kinematic friction coefficient

τ_L (s) : Langevin relaxation time of the contact line ($\equiv m / \zeta$)

τ_B (s) : Langevin relaxation time due to the viscous friction in the bulk of the liquid

ω (Hz) : Frequency of vibration

ω_0 (Hz) : Resonance frequency of eigen mode.

$\omega^*(\equiv \sqrt{\gamma/m})$ (Hz) : Fundamental frequency of vibration

$\sigma(V)$ ($\equiv V/|V|$) : Signum function of velocity

Δ (m/s^2) : First-order nonlinear friction force

A (m) : Amplitude of oscillating time-varying force $F(t)$

A_0 (m/s) ($\equiv A\omega_0$)

δ : Phase shift

V_1 (m/s) : Velocity of the contact line of the drop

$\varphi(=V_1/\tau_L^* - V_1/\tau_L - \sigma(V)\Delta)$ (m/s^2) : Difference term used for effective linearization

V_d (m/s) : Drift velocity

\bar{f} (m/s) : Externally applied fixed bias on the drop in terms of acceleration

\mathcal{A} (m^2) : Area under the liquid drop in contact with substrate

β (s/m) : Fitting parameter in the function $\tanh(\beta V)$

$\langle x \rangle$ (m) : Average drift or mean position of displacement

$\langle x^2 \rangle$ (m^2) : Variance of the displacement

P or $P(V)$: probability density function

D (m^2/s) : Diffusivity

μ (s/kg) : Mobility

T_{eff} (J) : Effective temperature

σ (S/m): Electronic conductivity in non-crystalline solids

T (K) : Temperature

ΔT (K) : Degree of subcooling, i.e the difference between the temperature of steam and that of the surface

J_q (J/m²s) : Heat flux

\dot{m} (kg/m²s) : Condensate flow rate

H_m (J/kg) : Latent heat of vaporization of water per unit mass

H_v (J/m³) : Latent heat of vaporization of water per unit volume

k_m (W/mK) : Thermal conductivity of the metal block

k_w (W/mK) : Thermal conductivity of water

B_1, B_2 : Constants

J (1/s) : Diffusive current of the coalesced drops

L_1 (m) : Width of hydrophobic strip

L_2 (m) : Length of hydrophobic strip

Σ (1/m²): Density of drops per unit area

B. Spring Constant of a Drop on a Surface

In order to find an expression for the spring constant of a spherical cap of a liquid drop (radius R , surface tension γ_{lv}) on a solid substrate, let us start with the total energy (U) of the system:

$$U = \frac{2\pi\gamma_{lv}R^2}{1 + \cos\theta} + \pi(\gamma_{sl} - \gamma_{sv})R^2 \quad (\text{B1})$$

Here, γ_{sv} and γ_{sl} are the surface free energies of the solid-vapor and solid-liquid interfaces respectively. We now expand U in Taylor series about the state of equilibrium energy U_o :

$$U = U_o + \left. \frac{\partial U}{\partial R} \right|_v (R - R_o) + \frac{1}{2} \left. \frac{\partial^2 U}{\partial R^2} \right|_v (R - R_o)^2 + \dots \quad (\text{B2})$$

Since the volume (v) of the drop is constant, we have a relationship between the radius of the drop and its contact angle θ as follows:

$$R \frac{d\theta}{dR} = -(2 + \cos \theta) \sin \theta \quad (\text{B3})$$

Using equation B3, equation B2 becomes:

$$\begin{aligned} U = & U_0 + 2\pi R(\gamma_{\ell v} \cos \theta + \gamma_{sl} - \gamma_{sv})(R - R_o) \\ & + 2\pi\gamma_{\ell v}(\sin^2 \theta(2 + \cos \theta))(R - R_o)^2 / 2 \end{aligned} \quad (\text{B4})$$

At equilibrium ($\partial U / \partial R = 0$), we have the Young's equation: $(\gamma_{\ell v} \cos \theta + \gamma_{sl} - \gamma_{sv}) = 0$. The spring constant is given by equation B5:

$$k_s = 2\pi\gamma_{\ell v} \sin^2 \theta (2 + \cos \theta)$$

or

$$k_s = \gamma_{\ell v} f(\theta) \quad (\text{B5})$$

It is well-known that equation B1 admits a parabolic energy profile. Now on the top of that, we superimpose a perturbation due to heterogeneity. An approximate way to introduce this perturbation is to consider a rough surface with the following profile: $y = y_o \sin kx$, k being the wave number. The maximum value of the surface area scales as $y_o^2 R / \lambda^2$ with a corresponding energy as $\beta y_o^2 R / \lambda^2$, where β is a constant (like a spring constant) that multiplied by y_o^2 gives an energy scale ($u_o = \beta y_o^2$) of heterogeneity. Another way to look at the problem is to define a pinning energy of magnitude u_o to a defect. If the distance between defects is λ , the total defect energy of an annulus of radius R^\pm and width dR^\pm is $\sim \pm (u_o / \lambda^2) R^\pm dR^\pm$. We balance $(u_o / \lambda^2) R^\pm$ with $\pm k_s (R - R_o)$ to obtain the relation: $R^\pm - R_o \sim \pm (u_o R^\pm / k_s \lambda^2)$, which is

equation 5 of the text. The physics of disorder deals with a length scale¹⁻³, called the ‘‘Larkin Length’’ or \mathcal{L} , which, in our problem is $\mathcal{L} \sim (k_s \lambda^2 / u_0)^2 \lambda$. When the Larkin length is much larger than the defect correlation length (λ), the contact line fluctuates sufficiently to probe different defects and the hysteresis decreases. Metastable states manifest when $\lambda \geq \mathcal{L}$. Using experimental data and equation 5, we estimate that λ is on the order of \mathcal{L} in our problem.

C. Brownian Motion with Non-linear Friction

The Langevin equation for the velocity (V) of an object subjected to a bias \bar{f} and a random force $f(t)$, is given as follows:

$$\frac{dV}{dt} + \frac{V}{\tau} + \sigma(V)\Delta = \bar{f} + f(t), \quad (\text{C1})$$

$$\frac{dx}{dt} = V,$$

Where τ is the Langevin relaxation time and Δ is the hysteresis force per unit mass that is equal to $\Delta \sim \gamma_w (\cos \theta_r - \cos \theta_a) / \rho R^2$ for a water drop, ρ being its density. The signum function $\sigma(V)$ indicates that the friction force changes sign with the direction of motion. An equivalent continuum version of equation C1 is the Klein-Kramers^{4,5} equation:

$$\frac{\partial P(\mathbf{x}, V, t)}{\partial t} = \left(-\nabla \cdot \mathbf{V} + \bar{f} \frac{\partial}{\partial V} + \frac{1}{\tau} \frac{\partial}{\partial V} \cdot \mathbf{V} + \Delta \frac{\partial}{\partial V} \cdot \frac{\mathbf{V}}{V} + \frac{K}{2} \frac{\partial^2}{\partial V^2} \right) P(\mathbf{x}, V, t) \quad (\text{C2})$$

For a spatially homogeneous steady state situation, the probability density function $P(V)$ of the velocity fluctuation can be obtained⁴⁻⁶ from equation C2 or simply from the balances of fluxes in the velocity space as follows:

$$\frac{K}{2} \frac{\partial P}{\partial V} + \Delta \frac{|V|}{V} P + \frac{VP}{\tau_L} = \bar{f} P \quad (\text{C3})$$

The solutions of the equation (C3) in the absence of a bias shows that $P(V)$ has both a Gaussian and an exponential components.

$$P(V) = P_o' \exp\left(-\frac{V^2}{K\tau_L} - \frac{2|V|\Delta}{K}\right) \quad (\text{C4})$$

The corresponding displacement fluctuation (x) is also non-Gaussian. One important parameter that is shown in equation 11 of the text (equation C5, here) is the effective relaxation time τ_L^* .

$$\frac{1}{\tau_L^*} = \frac{1}{\tau_L} + \frac{\Delta \langle |V| \rangle}{\langle V^2 \rangle} \quad (\text{C5})$$

Evaluation of both $\langle |V| \rangle$ and $\langle V^2 \rangle$, however, require a probability distribution of velocity that is given by equation (C4). We thus obtain:

$$1/\tau_L^* = 1/\tau_L + \Delta^2/K \quad (\text{C6})$$

Experimentally, we observed that the probability density function of displacement fluctuation can be expressed in terms of a stretched Gaussian equation of the form⁶:

$$P(x) = P_o \exp\left\{-\left[(x - x_p)/\sigma\right]^m\right\} \quad (\text{C7})$$

Here, x_p displacement corresponding to the peak value of $P(x)$, and σ is the standard deviation of x . The exponent m is equal to 2 for a Gaussian distribution, but it is usually less than 2 for a non-Gaussian distribution. In our experiments, we found that the displacement pdf is nearly symmetric with a value of $m < 2$ at short times. But the distribution becomes asymmetric at long time, each branch of which can be fitted with equation C7. We note that for a dynamics governed by a linear friction and a Gaussian white noise, the distribution should be symmetric Gaussian at

all time-scales. A skewed Gaussian distribution as found in our experiments results from non-linear Δ and a bias. In extending this type of stochastic model to the coalescence induced diffusive motion, one has to be careful that the noise inducing such a motion is far from being random Gaussian. Among other things, one expects that there will be a pause time between two coalescence events, which will have a certain distribution. Long ago, it was pointed out by Montroll⁷ et al that an unconventional statistics could result from such types of stochastic processes. Non-linear friction coupled with a non-Gaussian noise are expected to give rise to additional complexities.

D. Instability of the Adsorbed Film of Water

Consider a thin film of water of thickness ℓ on a solid substrate. The free energy of interaction of the vapor (1)-water(3) and the water (3)-substrate(2) interfaces can be expressed using Lifshitz theory as follows:

$$\Delta F_{132}(\ell) = \frac{k_B T}{\pi c^3} \int_{p=1}^{\infty} \sum_{n=0}^{\infty} \varepsilon_3^{3/2} \omega_n^2 \int_{\ell}^{\infty} p^2 \left[\frac{\exp(2p\omega_n \ell \varepsilon_3^{1/2} / c)}{\Delta_1 \Delta_2} - 1 \right]^{-1} dp d\ell \quad (D1)$$

$$\text{with, } \Delta_1 = \frac{\varepsilon_1(i\omega_n) - \varepsilon_3(i\omega_n)}{\varepsilon_1(i\omega_n) + \varepsilon_3(i\omega_n)}, \quad \Delta_2 = \frac{\varepsilon_2(i\omega_n) - \varepsilon_3(i\omega_n)}{\varepsilon_2(i\omega_n) + \varepsilon_3(i\omega_n)} \quad \text{and} \quad \omega_n = \frac{4\pi^2 n k_B T}{h} \quad (D2)$$

Here, k_B is the Boltzmann constant, h is the Planck's constant, T is the absolute temperature, c is the speed of light in vacuum, p is an integration parameter and n is a quantum number associated with the frequency of thermal photon ω_n . The zero frequency term in equation D1 is to be multiplied by $1/2$. ε_i are the dielectric permittivities expressed in the complex frequency axis $i\omega_n$:

$$\varepsilon(i\omega_n) = 1 + \frac{2}{\pi} \int_0^{\infty} \frac{\omega \varepsilon''(\omega) d\omega}{\omega^2 + \omega_n^2} \quad (D3)$$

Where, $\varepsilon''(\omega)$ is the loss component of the frequency dependent dielectric permeability $\varepsilon(\omega)$.

From equation D2, it is evident that the sign of the interaction, i.e. whether it is attractive or

repulsive depend on the sign of the product $\Delta_1\Delta_2$, which depends on the frequency of the photon contributing to interaction. A simple rule is that the interaction will be repulsive if the dielectric permeability follows either of the sequences, $\epsilon_1 > \epsilon_3 > \epsilon_2$ or $\epsilon_1 < \epsilon_3 < \epsilon_2$. This condition, i.e. $\epsilon_{air} < \epsilon_{water} < \epsilon_{substrate}$, is satisfied for air-water-substrate interfaces in the high frequency range (ultraviolet to x-ray region). However, the interaction will be attractive if the above sequence is broken, which is the case in the low frequency interaction of the vapor-water and the water-substrate interfaces, since $\epsilon_{air} < \epsilon_{water} > \epsilon_{substrate}$. Overall interaction is contributed by all the frequencies ranging from zero to x-ray range. However, as the high frequency interaction dominates for very thin films, we expect that the corresponding interaction of the vapor-water and water-substrate interfaces would be repulsive. If this interaction overwhelms the hydrophobic attraction across the vapor-water and water-substrate interfaces, the water film

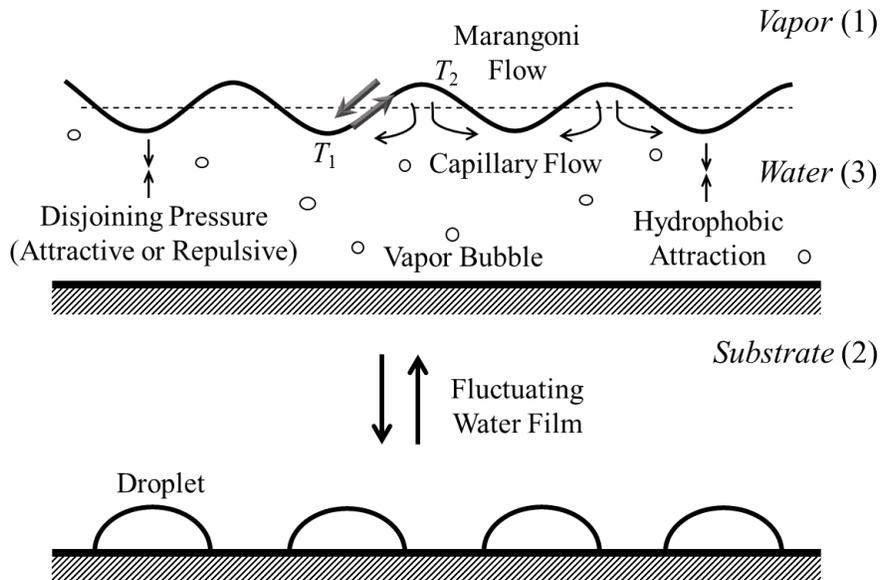


Figure S1. Schematic of different forces acting on a thin film of water in contact with a solid substrate. The Marangoni flow, depending upon its origin, can either stabilize or destabilize the perturbation of the surface.

could be stable and thus it will grow. However, as the film continues to grow via condensation of vapor, it will reach to a certain thickness, when the effect of retardation (the exponential term in equation D1) due to finite speed of light will frustrate the repulsive interaction arising from the high frequency photons. Only the low frequency photons will contribute for thick films and the interaction will be attractive. Thus, if the thickness of the film overshoots due to condensation, such a film will be unstable. Now consider a perturbation to the film as shown in figure S1. If there is a non-negligible resistance to heat transfer from vapor to the liquid (e.g due to non-condensable gases) , the temperature (T_1) of the surface of the thinner part of the film will have a different temperature than that (T_2) of the thicker part. If the vapor and the liquid are absolutely pure and there is no resistance to lateral heat conduction on the surface, T_1 should be less T_2 . In that case, thermal Marangoni flow will tend to stabilize the surface. However, if the vapor phase has binary components, e.g. water-methanol mixture, then due to differential concentration of one of the components, Marangoni flow could occur from the thinner to the thicker part of the film, which will increase the surface perturbation. We suspect T_1 could be greater T_2 in some special cases when the heat transfer resistance in the later direction on or near the surface is significant, resulting in a surface Marangoni flow that would favor the growth or perturbation. In all cases, the differential Laplace pressure between the convex and concave parts of the surface will tend to stabilize the surface. However, when the film thins enough, a strong hydrophobic attraction (which varies exponentially with thickness) across the vapor-water and water-substrate interfaces could dominate the interaction and the film would thus break up (this is, perhaps, the strongest force behind the instability of a thin film on a non-wetting surface). The breakup of such a film could also be aided if small vapor bubbles are present in the film that will grow by

nucleation. The net result is that the water film could grow to a certain critical thickness, which would ultimately break up leading to a fluctuating water film on the substrate.

E. Additional Citations

Because of the limited numbers of references allowed for this article, we were not able to discuss all the works relevant to our subject. We make an effort to cite some of the references here.

A detailed review of the various methods to prepare surface chemical gradients can be found in reference 12. The effect of vibration in the mitigation of hysteresis as studied by other investigators can be found in references 13 to 18. The origin of non-linearity due to the coupling of horizontal and vertical vibration can be found in various modes of shape fluctuations arising from the coalescence of two drops are reported in reference 19.

Elastic force induced motion of a drop was reported in an interesting paper by Style²⁰ et al. Some relevant studies on the attraction and motion of particles by elastic forces in a gel and a membrane were reported in 21 to 23. A recent reference to noise induced critical dynamics can be found in ref 24. We also point out a recent interesting study in water collection²⁵ using the coalescence of condensed drops.

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