Electronic Supplementary Material (ESI) for Soft Matter

Supplementary materials

Flow triggered by instabilities at the contact line of a drop containing nanoparticles

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Movie S1: Evaporation of water droplets containing 8 μm glass microspheres and 3 wt% silica nanoparticles. This movie corresponds to the data in Fig. 1(a) & 1(b). **Top panel:** Drying of the drop filmed from the side. **Bottom panel:** Drying of the drop filmed at identical time points from the bottom. The droplet depins at about 33 s, and shortly thereafter, all microspheres move towards the center of the drop. The sphere at the edge of the drop has a larger maximum velocity. At about 42 s, the contact line repins.

Movie S2: Evaporation of 0.1 M NaCl droplets containing 8 μm glass microspheres and 3 wt% silica nanoparticles. This movie corresponds to the data in Fig. 1(c). **Top panel:** Drying of the drop filmed from the side. **Bottom panel:** Drying of the drop filmed at identical time points from the bottom. The contact line in this drop does not depin and the microspheres do not move.

Movie S3: Evaporation of water droplets containing 8 μm glass microspheres and no silica nanoparticles. This movie corresponds to the data in Fig. 1(d). **Top panel:** Drying of the drop filmed from the side. **Bottom panel:** Drying of the drop filmed at identical time points from the bottom. When the receding contact line reaches a microsphere it transports the microsphere. Only the spheres at the contact line begin moving.

Effect of concentration of large diameter (10 nm) nanoparticles on microsphere speed: The effect of concentration of large (10 nm), nanoparticles on microsphere speed is similar to the smaller (5 nm) nanoparticles [Fig. 3(a)], though less pronounced. Microsphere speed decreases with increasing concentration of nanoparticles [Fig. S1],

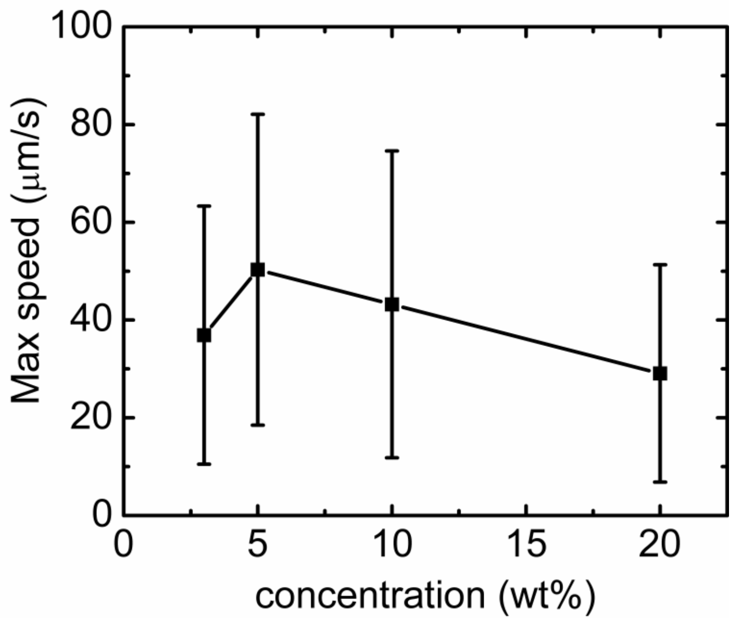

FIG. S1. Mass transport speed depends on nanoparticle concentration. Microsphere speed decreases as the concentration of 10 nm nanoparticles increases

Internal Circulation and Flow in the Drops

Impulsive velocity changes due to successive pinning-depinning of the contact-line drive acoustic waves into the droplet and establish a circulating fluid flow. The acoustic waves accelerate the toroidal circulation in the droplet until a balance between energy input and viscous dissipation is reached. The rate of energy input is $2\pi R\gamma v_R$, i.e., the work done by the surface tension force per unit time, where R is the radius of the drop and v_R is the contraction speed. The rate of energy dissipation can be estimated as,

$$\varepsilon\left(\frac{m_d v_{circ}^2}{2}\right)\left(\frac{v_{circ}}{2\pi(R/2)}\right) = \frac{\varepsilon}{2\pi}\left(\frac{m_d v_{circ}^3}{R}\right) \qquad (1)$$

where ε is an efficiency factor, the first term in the left hand expression is the kinetic energy of circulation and the second bracketed expression is the circulation turnover timescale. The velocity v_{circ} is the average circulation velocity over the whole mass of the droplet, m_d. Setting the energy input equal to the dissipation estimate of Eq. 1 we get,

$$\varepsilon v_{circ}^3 = \left(\frac{4\pi^2 R^2 \gamma}{m_d}\right) v_R, \text{or,} \quad v_{circ} = \frac{1}{\varepsilon}\left(v_\gamma^2 v_R\right)^{1/3} \qquad (2)$$

In this equation v_R is the edge contraction velocity.

To make quantitative estimates of the microsphere speed and acceleration, we begin by considering the acceleration of the spheres by the flowing fluid. This is described by the classical Stokes equation,

$$\frac{dv}{dt} = \frac{-6\pi R_s \eta}{m_s}\left(v - v_{flow}\right) = \frac{v_{flow} - v}{\tau_d} \qquad (3)$$

where v is the microsphere velocity, v_{flow} is the speed of the background fluid, m_s, R_s are the mass and radius of the microsphere, and η is the fluid viscosity coefficient. The factor τ_d is the drag timescale or the microsphere acceleration timescale.

The Stokes equation is usually used in the context of a constant velocity fluid flow, but while energy is input, and before the input/dissipation balance of Eq. 2 is reached, the circulation is accelerated. Specifically, if we assume that all the input energy goes into the kinetic energy of the circulation, we can describe the acceleration as,

$$dK = 2\pi\gamma R dR, \text{or}, \quad -\frac{m_d v_{circ}^2}{2} = \pi\gamma\left(R^2 - R_o^2\right) \qquad (4)$$

where K is the kinetic energy of the circulation, and R_o is the (initial) radius of the droplet at the start of this phase. An expression for v_{circ} as a function of time can be derived with the substitution, $R = R_o - v_R t$. The result can be written,

$$\frac{v_{cir}}{v_f} = \sqrt{2\frac{t}{\tau_1} - \left(\frac{t}{\tau_1}\right)^2} \qquad (5)$$

with $\tau_1 = R_o / v_R$, and v_f given by Eq. 3 above. Note that when $t = \tau_1$, then $v_{circ} = v_f$, and so v_f is the "final" velocity.

The pinning-depinning events work cumulatively against drag described by Eq. 3. Thus, we can identify v_{circ} with v_{flow} and substitute Eq. 5 into Eq. 3, yielding

$$\tau_d \frac{dv}{dt} = v_{circ} - v = v_f \sqrt{2\frac{t}{\tau_1} - \left(\frac{t}{\tau_1}\right)^2} - v \qquad (6)$$

This differential equation has a smooth and slowly varying solution that is numerically integrable. It has a solution of the form,

$$v = v_f \sqrt{2\frac{t}{\tau_1} - \left(\frac{t}{\tau_1}\right)^2} \sum_{p=1}^{n} c_p \left(\frac{t}{\tau_1}\right)^p \tag{7}$$

where retaining terms of order n yields a solution accurate to order $(t/\tau_1)^{n-1}$.

The circulating fluid flow reaches a balance when the energy input equals viscous dissipation. The simplest approximation for the circulation flow along a radius in the droplet is a quadratic function of the form, $v = b - a(r - r_{max})^2$, where a and b are constants, and r_{max} is the radius where the circulation is the most horizontal. For a fluid element initially located at some $r > r_{max}$, and which subsequently travels to the center, we adopt the boundary conditions: $v = 0$ at $r = 0$, and $v = v_{max}$ at $r = r_{max}$. Then the velocity profile of the radial component of the circulation can be written as,

$$\frac{v}{v_{\max}} = 1 - \left(\frac{r}{r_{\max}} - 1\right)^2 \tag{8}$$

This equation can be integrated to obtain,

$$\frac{r}{r_{\max}} = \frac{2\exp\left(\frac{2(t - t_{\max})}{\tau_{\max}}\right)}{1 + \exp\left(\frac{2(t - t_{\max})}{\tau_{\max}}\right)} \tag{9}$$

where we have integrated from some arbitrary time t along the trajectory to the time t_{max} when $r = r_{max}$. The timescale $\tau_{max} = r_{max}/v_{max}$. Eq. 9 can be substituted into Eq. 8 to obtain the dependence of fluid element velocity on time,

$$\frac{v}{v_{\max}} = 1 - \left[\frac{\exp\left(\frac{2(t - t_{\max})}{\tau_{\max}}\right) - 1}{\exp\left(\frac{2(t - t_{\max})}{\tau_{\max}}\right) + 1} \right]^2 \qquad (10)$$

The net flow of a microsphere is a combined response to the driving forces of the accelerating (Eq. 7) and balanced (Eq. 10) circulation, mediated by the Stokes drag. Eq. 10 was derived to describe the fluid flow near bottom of the droplet. The fact that, with the right set of parameter values, it fits the peak of the microsphere speed *vs.* time data (Fig. 1(b)) means that the spheres' generally slower motion and delayed response due to damping is well approximated by the same function form.

Based on these considerations we adopt a simple model for the spheres motion consisting of the sum of the contributions from Eqs. 7 and 10,

$$v = v_f \sqrt{2\frac{t}{\tau_1} - \left(\frac{t}{\tau_1}\right)^2} \sum_{p=1}^{n} c_p \left(\frac{t}{\tau_1}\right)^p + v_a \left\{ 1 - \left[\frac{\exp\left(\frac{2(t - t_a)}{\tau_a}\right) - 1}{\exp\left(\frac{2(t - t_a)}{\tau_a}\right) + 1} \right]^2 \right\} \qquad (11)$$

The subscript *max* in Eq. 10 (for the fluid flow), has been replaced with subscript *a* for a microsphere.

Estimating depinning time and energy released by contact line hopping

The contact line hops much faster that the time required for an acoustic pulse to travel from the edge to the center of the drop. The energy released by a single depinning-pinning cycle is given by

$$\Delta E = 2\pi R \Delta R \gamma \qquad (12)$$

where ΔR is the distance moved by the contact line. This event drives a mass of fluid, $\rho 2\pi R \Delta R h$, inwards with a velocity v. The velocity of the fluid flow depends on the height of the depinned fluid column; it has maximum velocity $v_{R_{single}}$ at the contact line and decays rapidly with height reaching zero velocity at the top of droplet h_1. Assuming that the velocity decays linearly with h, the energy due to inward fluid flow is given by

$$\Delta E = \rho \pi R \Delta R \int_0^{h_1} \left(v_{R_{single}} - \frac{h}{h_1} v_{R_{single}} \right)^2 dh = \rho \pi R \Delta R \frac{v_{R_{single}}^2 h_1}{2} \qquad (13)$$

Setting this equal to the energy released by a single depinning-repinning cycle, we get

$$v_{R_{single}} = \sqrt{\frac{6\gamma}{\rho h_1}} \qquad (14)$$

For γ = 0.073 N/m and $h_1 \sim$ 100 μm, $v_{R_{single}}$ = 2.1 m/s. It is important to note that this calculated value corresponds to the contact line velocity of a single depinning-repinning cycle and not v_R which is the average contact line velocity over the entire series of pinning-depinning events (Fig. 1b). Furthermore, $v_{R_{single}}$ is likely underestimated in this calculation since the velocity of fluid flow decreases more rapidly with height than described by a simple linear relationship.

Once the contact line depins, it will be repinned again at the next line of the nanoparticles; ΔR is therefore approximately the diameter of the nanoparticles. The depinning-repinning time interval $\Delta t_{contacttime} \approx \frac{5\,nm}{2\,m/s} = 2.5\,ns$. However, the time for the acoustic wave to travel from the edge of the droplet to the center of drop can be estimated to be $\Delta t_{acoustic} = \dfrac{R}{speed\ of\ sound} \approx 0.3\ \mu s$. Since $\Delta t_{contact\ line}$ is much smaller than $\Delta t_{acoustic}$, impulsive velocity changes due to successive pinning-depinning of the contact-line can drive acoustic waves into the droplet and establish a circulating fluid flow.

There is enough energy contained in the entire series of pinning-depinning cycles to drive the circulatory fluid flow. The kinetic energy required to drive all the fluid in the droplet with R ~ 500 μm into a circulating flow with v_{circ} ~100 μm/s (Figure 1b), can be estimated as $\left(\dfrac{m_d v_{circ}^2}{4}\right) \approx \dfrac{\rho \pi R^2 h_1 v_{circ}^2}{2} \approx 2 \times 10^{-16}\ J$. On the other hand, the energy input due to the entire series of pinning-depinning cycles across the gel foot (ΔR ~ 100 μm) is given by $2\pi R \Delta R \gamma \approx 2 \times 10^{-8}\ J$; this energy is much larger than the energy needed to establish the circulatory fluid flow.