1. Supplemental figures

Figure S1. Top: 3D view and cutaway of sample cell. Bottom: schematic cross-section. Sample cells are designed to retain a thin film of the aqueous phase beneath a well of oil. The region between the bottom glass and the PEEK lip draws the aqueous phase in when we initially fill the cells, pinning the edges of the film. This layer is between 30 and 100 µm thick, well within the working distance of our objective. The top coverslip is held in place by capillary action.

2. Supplemental discussion

2.1. Approach hydrodynamics. To calculate the hydrodynamic drag on a particle as it approaches the interface, we treat the interface as a shear-free boundary. This approximation is justified by the large viscosity ratio; the viscosity \( \eta \) of the...
aqueous phase is 11.5 mPa-s, while that of decane is about 0.9 mPa-s. Following H. Brenner\(^1\), we write the modified Stokes drag on the particle as

\[ F_d = \beta 6\pi \eta R v \]  \hspace{1cm} (S1)

where \( R \) is the radius of the particle and \( v = \frac{dz}{dt} \) is the velocity component normal to the interface. \( \beta \) is the boundary correction, given by

\[
\beta = \frac{4}{3} \sinh \delta \sum_{n=1}^{\infty} \frac{n(n+1)}{(2n-1)(2n+3)} \times \left[ \frac{4 \cosh^2([n+\frac{1}{2}]\delta) + (2n+1)^2 \sinh^2(\delta)}{2 \sinh((2n+1)\delta) - (2n+1) \sinh(\delta)} - 1 \right] \]  \hspace{1cm} (S2)

where \( \delta = \cosh^{-1}(1 - z/R) \). We retain 100 terms in this series to prevent numerical artifacts when fitting.

Because \( \beta \) does not have a simple analytic form, we discretize Equation S1 as

\[ \Delta z = \frac{F_p}{6\pi \eta R \beta(z_{\text{int}} - z)} \Delta t \]  \hspace{1cm} (S3)

where \( F_p \) is the magnitude of the force from the radiation pressure. At the low Reynolds number of the experiment, this should be equal to \( F_d \). We then have the recurrence relation

\[ z_{i+1} = z_i + \frac{F_p}{6\pi \eta R \beta(z_{\text{int}} - z_i)} \Delta t \]  \hspace{1cm} (S4)

We compare the values of \( z_i \) at times \( i\Delta t \) to the measured values of \( z \) for each frame. The fit parameters are \( F_p \), \( z_{\text{int}} \), and \( z_0 \), an arbitrary offset.

2.2. Equation of motion. To derive the evolution equation for the centre of mass of the particle, we first deduce the interfacial forces driving the system towards equilibrium, then we consider two mechanisms for the motion of the contact line. The first is based on viscous damping associated with flow near the contact line and the second on activated hopping of the contact line over surface defects. Models for these two mechanisms have been used to analyse many dynamic wetting phenomena\(^2\). We find that the purely hydrodynamic mechanism fails to explain the extremely low velocities (\( \dot{z} \approx 10^{-7} \) m/s) and the approximately logarithmic behaviour observed in the experiments.

2.2.1. Forces and degrees of freedom. As noted in the main text, body forces such as buoyancy and optical trap pressure are negligible compared to interfacial forces. Since the particle-interface system is isolated and cannot impose a force on itself, the interface must remain flat.

Because the damping should be dominated by effects near the contact line, we place ourselves in the reference frame of the particle and derive the force on the contact line and its ensuing motion. The magnitude of the force per unit length \( F_{cl} \) on the contact line, which causes it to move down the particle, is related to the three interfacial tensions, \( \gamma_{po} \), \( \gamma_{pw} \), and \( \gamma_{ow} \), where the subscript \( o \) stands for “oil”, \( w \) for “water” (or the aqueous phase) and \( p \) for “particle” (see Fig. S2):

\[ F_{cl}(t) = \gamma_{ow} \cos \theta_D(t) + \gamma_{pw} - \gamma_{po} \]  \hspace{1cm} (S5)
The force is tangent to the particle surface. When the particle is in equilibrium with the interface this reduces to the Young-Dupré equation:

\[ \cos \theta_E = \frac{\gamma_{po} - \gamma_{pw}}{\gamma_{ow}}. \]

We can therefore rewrite Equation S5 as

\[ F_{cl}(t) = \gamma_{ow} (\cos \theta_D(t) - \cos \theta_E) \]  

(S6)

There are three degrees of freedom: the dynamic contact angle \( \theta_D \), the polar angle \( \alpha \), and \( z \). Because the interface is flat, \( \alpha = \theta_D \) and \( z = R(1 - \cos \alpha) \). Thus there is only one degree of freedom remaining, \( \theta_D \). Because we are at low Reynolds number (\( Re \lesssim 10^{-3} \)), the instantaneous work done by the driving force \( F_{cl} \) must be balanced by the damping. We can therefore use a power balance to find the time evolution \( \dot{\theta}_D \) of the one degree of freedom. Comparing the resulting predictions of the characteristic particle velocities and the shapes of trajectories with the experiments allows us to distinguish between alternative damping mechanisms.

2.2.2. *A hydrodynamic mechanism for damping.* The geometry of the interface and particle can lead to a dramatic enhancement of the viscous drag on the sphere, particularly at short times when the contact angle is small. As shown in Fig. S3, the drag is associated with flow from a wedge of fluid near the particle. This flow
dominates the dissipation because fluid must leave a highly confined region. Thus the dissipation should diverge as the width of the wedge decreases. It is therefore conceivable that at short times the enhanced viscous drag might account for the small capillary numbers (Ca ≈ 10^{-4}).

There are two modes of fluid flow generated as the particle moves: 1) the contact line can slip past the particle with velocity $R\dot{\alpha}$, where $R$ is the radius of the sphere and $\dot{\alpha}$ the angular velocity; and 2) the contact angle can open out with velocity $R\dot{\theta}_D$. Because the interface is flat the two angular velocities are equivalent. Analysing each mode independently leads to the following estimate for the viscous dissipation within the wedge for small angles.

$$TS \approx \frac{\eta (R\dot{\theta}_D)^2}{\theta_D^\xi}$$  \hspace{1cm} (S7)

where $\eta$ is the viscosity of the aqueous phase and $\xi \geq 1$ is the divergence associated with moving fluid out of a highly confined region. The exponent of the pure slip mode has been determined² to be $\xi = 1$. The exponent corresponding to the pure bending mode will be the subject of a later paper; its value does not affect our analysis. We neglect the oil’s contribution to the viscous dissipation in Equation S7 because the viscosity ratio is large: $\eta_{\text{aqueous}}/\eta_{\text{oil}} > 10$. Below, we employ the above small-angle approximation of hydrodynamic dissipation and compare to experiment.

Our fluids are not completely wetting and hence we utilize the entire expression for the force on the contact line, Equation S6, in the power balance:

$$R\dot{\theta}_D \gamma_{\text{ow}} (\cos \theta_D - \cos \theta_E) = \frac{\eta (R\dot{\theta}_D)^2}{\theta_D^\xi}$$  \hspace{1cm} (S8)

Simplifying further we have:

$$R\dot{\theta}_D = \frac{\gamma_{\text{ow}}}{\eta} \theta_D^\xi (\cos \theta_D - \cos \theta_E)$$  \hspace{1cm} (S9)

The velocity of the particle can be determined from trigonometry: $z = R(1 - \cos \theta_D)$, and inserting this expression into the power balance gives us:

$$\dot{z} = \frac{\gamma_{\text{ow}}}{\eta} \theta_D^\xi (\cos \theta_D - \cos \theta_E) \sin \theta_D$$  \hspace{1cm} (S10)

Since $\xi > 0$ and $\theta_D > \theta_E$ the above expression corresponds to positive velocities of the particle. However, as the contact angle increases, decreasing dissipation ($\dot{\theta}_D$) and decreasing force on the particle $(\cos \theta_D - \cos \theta_E)$ have countering influences on the motion. The particle first accelerates and then relaxes towards equilibrium.

We can estimate the dynamic contact angle at which the transition from acceleration to relaxation occurs by determining when $\dot{z} = 0$. Assuming an equilibrium contact angle of $\theta_E = \pi/2$, a reasonable approximation for the polystyrene spheres we investigate, we find a threshold value of $\theta_D \approx 1 \approx 60^\circ$. The measured trajectories show no acceleration even at contact angles as low as 20–30°. Furthermore, for large contact angles, $\theta_D \gtrsim O(1)$, the analysis predicts that $\dot{z} \approx \gamma_{\text{ow}}/\eta \approx 3 \text{ m/s}$, seven orders of magnitude larger than what is observed. The hydrodynamic model fails to explain (a) the decrease in velocity with time; (b) the magnitude of the velocity at later times; and (c) the apparent logarithmic particle trajectory. Thus
hydrodynamic dissipation plays no detectable role in determining the relaxation behaviour of interfacial particles.

**Figure S4.** Close up of contact line near the surface. The contact line must hop over defects of typical scale $A$.

### 2.2.3. Activated hopping mechanism.

An alternative mechanism for the damping takes into account the progression of the contact line over surface heterogeneities, either physical or chemical (Fig. S4). As shown in the main text, a model incorporating thermally-activated motion of the contact line explains all aspects of the relaxation. Here we derive the model in detail.

The premise is that the velocity of the contact line is related to the rate at which it hops over defects. Consider a contact line pinned by surface defects of average area $A$. The probability of hopping over a defect depends on the activation energy, which depends on the driving force $F_{cl}(t)$. We can therefore write an Arrhenius equation for the velocity tangent to the sphere’s surface, $R\dot{\alpha}$:

$$R\dot{\alpha} = V_0 \exp\left(-\frac{U}{kT} + \frac{F_{cl}(t)A}{2kT}\right).$$

(S11)

where $kT$ is the thermal energy, $V_0$ encapsulates the molecular velocities, and $U$ is the energetic barrier from defects. This equation of motion neglects the hopping of molecules over surface defects in the “backwards” direction, that is, against the opposing force. This effect, although present, is significant only very close to equilibrium (section 2.2.4). Substituting for $F_{cl}$ from Equation S6, we find

$$R\dot{\alpha} = V_0 \exp\left(-\frac{U}{kT} + \frac{\gamma_{ow}}{R} \left(\cos \theta_D(t) - \cos \theta_E\right) \frac{A}{2kT}\right).$$

(S12)

We can then express the equation of motion in terms of the observable $z$ using the kinematic relation $R\dot{\alpha} = R\dot{z}/\sqrt{z(2R-z)}$:

$$\dot{z} = \nu \sqrt{z(2R-z)} \exp\left(-\frac{A\gamma_{ow}}{2kT} z\right).$$

(S13)

where $\nu = (V_0/R) \exp(-U/kT + [1 - \cos \theta_E] A\gamma_{ow}/2kT)$.

To discern the logarithmic behaviour, we return to Equation S12 and consider a perturbation expansion around the equilibrium value of the contact angle, $\theta_D = \theta_E - \epsilon$. The evolution equation for the dynamical variable $\epsilon$ is

$$\dot{\epsilon} \approx -\frac{V_0}{R} \exp\left(-\frac{U}{kT} + \frac{\gamma_{ow} A \sin \theta_E}{2kT} \epsilon\right).$$

(S14)
We can express this in terms of $z$ using $\sin \theta_E \epsilon = (z_E - z)/R$:

$$\dot{z} \approx \nu R^* \exp \left( -\frac{A \gamma_{ow} z}{2RkT} \right)$$

(S15)

where $R^*$ is the equilibrium wetted radius. The particle trajectory close to equilibrium therefore follows

$$z \approx \frac{2RkT}{A \gamma_{ow}} \ln \left( \frac{A \gamma_{ow}}{2RkT \nu R^* t} \right)$$

(S16)

where $t$ is the time after the breach.

Fits to Equation S13 are highly sensitive to the value of $A$ but not sensitive to the value of $\nu$, which can vary over orders of magnitude; thus only the value of $A$ can be determined precisely from the fit. This is because $A$ is related to the slope of the trajectories plotted on semi-log axes (Fig. 1d), whereas the time constant $1/\nu$, which determines where the trajectory reaches equilibrium, is coupled sensitively to both $z_E$ and $A$. Physically, $1/\nu$ represents the timescale for the contact line to hop over a defect under zero force – in other words, close to equilibrium. We cannot obtain a precise measurement of $1/\nu$ because we cannot access this timescale in our experiments. But we can obtain a precise measurement of $A$ because it is related to the rate at which the velocity changes with force.

Unlike the hydrodynamic model, the activated hopping model of dynamic wetting reproduces the logarithmic behaviour in time and provides a mechanistic reason for the large relaxation times. Put simply, as the contact line slips, the particle rises but the driving force decreases; thus the effective activation energy increases, and the rate of hopping becomes smaller and smaller.

2.2.4. Correction close to equilibrium. In deriving Equation S13 we neglected the hopping of molecules in the backward direction, that is, against the driving force. But this term is not negligible when the system is very close to equilibrium. By considering the full equation of motion, with both forward and backward terms, we quantify the dynamic contact angle interval within which (S13) is valid.

Including the backward motion of the contact line alters the equation for the contact line’s velocity, Equation S11, to

$$R\dot{\alpha} = V_0 \exp \left( -\frac{U}{kT} \right) \left[ \exp \left( \frac{F_{cl}(t)A}{2kT} \right) - \exp \left( -\frac{F_{cl}(t)A}{2kT} \right) \right]$$

(S17)

$$= V_0 \exp \left( -\frac{U}{kT} + \frac{F_{cl}(t)A}{2kT} \right) \left[ 1 - \exp \left( -\frac{F_{cl}(t)A}{kT} \right) \right]$$

(S18)

Our use of Equation S11 is valid when the second term in square brackets is small in comparison to unity, $\exp \left( -2F_{cl}(t)A/kT \right) \ll 1$. This term’s contribution to the contact line’s velocity cannot be neglected when $2F_{cl}(t)A \approx kT$. We estimate the contact angle that satisfies this approximate equality by considering dynamic values of the contact angle sufficiently close to equilibrium, $\theta_D = \theta_E - \epsilon$, allowing us to approximate the contact line force as follows

$$F_{cl} = \gamma_{ow} \left( \cos (\theta_E - \epsilon) - \cos \theta_E \right)$$

(S19)

$$\approx \gamma_{ow} \epsilon \sin \theta_E$$

(S20)
Hence, equation S13 justifiably neglects the backwards term until when $\theta_E - \theta_D \approx kT/2\gamma_{ow} \sin \theta_E A$. For typical parameters of our system we estimate this deviation from equilibrium to be $\theta_E - \theta_D \approx 0.01$. This estimate makes apparent the accuracy of the simplified equation of motion S13.

2.3. Additional considerations.

2.3.1. Capillary waves. We have attributed the slow dynamics of a particle adsorbing at an interface to properties of the particle’s surface. Here we justify ignoring the dynamics of the liquid-liquid interface.

The motion of the particle can generate capillary waves that perturb the interface and the local contact angle in a dynamic manner. Since a model of the contact line hopping over surface heterogeneities finds good agreement with observations it is natural to expect waves with a characteristic wavelength comparable to the defect size to be generated. This could lead to the contact line force imposed on the particle to vary. Are capillary dynamics relevant to our system? Were the capillary waves significantly damped due to viscous effects, we could safely neglect interfacial dynamics and assume a static interface. Since we expect the dominant wavenumber to be set by the inverse defect size, we now consider the nature of viscous effects at these scales.

For a liquid-liquid interface, viscous effects are large enough to damp out perturbation above a critical wavenumber

$$k_c \sim \frac{\gamma \rho}{\eta^2}$$

where $\rho$ and $\eta$ are the density and viscosity of the water phase. We have neglected the density and viscosity of the oil phase because they are both substantially smaller than those of the water. Using relations that account for the viscosity and density differences does not change the order of magnitude of the calculations below.

Wavenumbers $k$ below $k_c$ satisfy $\omega_k \ll \eta k^2/\rho$, where $\omega_k = \sqrt{\gamma k^3/\rho}$ is the dispersion relation of capillary waves in an ideal fluid. Physically, this corresponds to waves that are damped before they can propagate. Estimating this critical wavenumber in our microscopic system gives $k_c \approx 10^7$ m$^{-1}$. Hence, wavelengths comparable to, and smaller than, the particle size itself ($10^{-6}$ m) are severely damped through viscous effects. In particular the capillary waves are exponentially damped in time with a characteristic timescale $\tau_{\text{damping}} = \eta/\gamma k$. Thus for $t \gg \tau_{\text{damping}}$ the perturbations to the interface are negligible. Evaluating this damping timescale at the inverse defect size (the dominant mode of capillary waves), we find $\tau_{\text{damping}} \approx 10^{-8}$ s. Because this is much smaller than the timescale $t$ over which the particle moves a distance equal to the defect size, we can justifiably neglect perturbations of the interface generated by the motion of the contact line past surface defects.

2.3.2. Capillary interactions between particles. In our analysis we dismissed the interactions between particles as a possible cause of the slow relaxation. This is because in our experiments the particle being observed was at least 30 µm away from other particles. Even when we observed multiple particles adsorb, as shown in Fig. 2, the particles were about 20 µm apart. We estimate that the strength of the gravity induced capillary interaction is on the order of $10^{-6}$ kT for particles 20 µm apart.
Stamou et al. consider how higher order multipole distortions of the interface may result in long-range interactions. Such interfacial distortions could be caused by contact line pinning around the contact line. If the distortions are on the order of 50 nm then the interaction energy between two particles 30 µm apart may be around $1kT$ depending on their orientation\(^6\). However, we have not noticed such a long-range attraction in our system, and the adsorption dynamics we observe do not depend on the interparticle separation.

**References**