

Diffusion from particle-coated drops: The subtle role of particle sizeAlexandros T. Oratis , Matteo Camagna , Timo J. J. M. van Overveld , and Valeria Garbin **Department of Chemical Engineering, Delft University of Technology,
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Many natural and industrial systems involve particle-laden interfaces. Because interfacial particles prevent the coalescence and coarsening of drops, they hold promise for various applications requiring stable emulsions. Despite their remarkable ability to stabilize emulsions, it remains challenging to characterize how particles influence the interfacial transport of dissolved solutes. Here we quantify the diffusion from a single particle-coated drop by confining it to a two-dimensional configuration. Using fluorescence microscopy, we extract the intensity profiles of the fluorescent dye as it diffuses from the drop, yielding spatiotemporal measurements of the concentration field. Over a range of particle sizes, the particles impose minimal resistance to diffusion. We explain this behavior with a mathematical model describing interfacial mass transfer across a particle-coated interface. The particle monolayer controls the temporal dynamics of interfacial flux, but hinders the overall transport only at extreme coverage fractions beyond the close-packing limit. This framework reveals why particles often fail to hinder diffusion, offering new pathways to harness mass transfer in particle-stabilized emulsions.

DOI: [10.1103/gpju-8nqr](https://doi.org/10.1103/gpju-8nqr)**I. INTRODUCTION**

Complex fluid interfaces involving colloidal particles appear in a variety of natural and industrial systems [1–3]. By adhering to an interface, particles reduce the surface free energy [4], altering the functional response of the liquid interface in terms of its rheology and rigidity [5,6]. In the context of drops and bubbles, interfacial particles prevent coalescence and coarsening, leading to remarkable stability of emulsions and foams [7–9]. The enhanced stability provided by particles has been exploited for a broad class of applications that require long-lasting emulsions, ranging from cosmetic products [9,10] and processed foods [11,12], to chemical conversion [13–16]. An important physical mechanism that dictates the performance of these systems involves the transport of solutes across the liquid interface. In food and cosmetic products it is advantageous to prevent diffusion, as dissolution and ripening of drops and bubbles can diminish the desired functional and sensory properties. In contrast, diffusion is critical for the exchange of reactants and products in chemical conversion [14] and drug release [17–19]. It is thus imperative to fundamentally understand how the presence of particles at the liquid interface affects the diffusion dynamics.

When particles adhere to interfaces, they reduce the overall surface area available for mass transport. When the particles are densely packed at the liquid interface, the pores through which solutes may diffuse become fewer or smaller in size. Because the diffusive flux is typically

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proportional to the surface area, this reasoning suggests that particles will impede the transport of solutes. Indeed, various experimental studies demonstrate that particles can dramatically affect diffusion-governed processes. For instance, particles will arrest the capillary-driven dissolution of bubbles [20] or form multilayers that slow down the evaporation of liquid marbles [21–23]. Yet these two model systems involve retracting interfaces, which significantly affect the diffusion rates by reducing the interfacial area. Conversely, in systems involving the diffusive exchange of solutes from drops with constant sizes, the effect of the particle layer remains ambiguous. While various studies report a strong hindrance on mass transport in the presence of a particle coating [24–26], others demonstrate a negligible effect [17,27–30]. These conflicting results highlight the need for systematically quantifying the effects of particle-coated interfaces on diffusion.

Our recent theoretical investigations on diffusion through planar interfaces coated with spherical particles demonstrated that the particles did not significantly influence mass transport [30,31]. The reduction in interfacial area available for diffusion induced by the particles does not limit the transport of dissolved solutes, unless the coverage fraction is increased to extreme values beyond the close-packing limit of spheres. A simple criterion based on the surface coverage and particle size can predict when the coating hinders diffusion, which is consistent with the experimental results reported in the literature [31]. Yet none of these experimental measurements were performed in model configurations to systematically examine the effects of the particle monolayer. Furthermore, the theoretical predictions are limited to transport between liquids with identical transport and thermodynamic properties. Therefore, a generalized and validated framework for diffusion from particle-coated drops is still lacking.

In this study we aim to quantify and generalize the diffusion dynamics from an isolated particle-coated drop into a surrounding liquid. We perform fluorescent microscopy experiments to characterize the diffusion dynamics across a wide range of particle sizes. We characterize the effects of the particles by measuring the radial extent to which the fluorescent dye penetrates the outer phase, as well as the time it takes to fully deplete the drop. In addition to the experiments, we perform finite-difference simulations on the diffusion across particle-laden interfaces. Our theoretical approach couples the coating, transport, and thermodynamic properties, whose collective effects can be captured by two dimensionless parameters. Our combined framework demonstrates that particle size has a subtle effect on the transport dynamics.

II. METHODS

A. Water-in-oil emulsions

Our experimental protocol closely follows the one previously adopted by our group [30], based on fluorescent microscopy imaging. We first generated coated drops by preparing particle-stabilized emulsions, consisting of water drops surrounded by hexadecane. We dispersed sulfate latex polystyrene (PS) beads (Invitrogen, Thermo Fisher Scientific) in water at a concentration of 2% w/v using ultrasonication for 5 minutes. The suspension was then mixed by equal volumes with a 2 mM Rhodamine B (RhB) solution, which acts as the fluorescent tracer to track the concentration field. A small amount of a salt (50 mM CaCl_2) was added to screen the electrostatic repulsion between the negatively charged polystyrene particles and promote their adsorption to the liquid interface during emulsification. The suspension was deposited in a vial with hexadecane at a volume ratio of 20:80 v/v. The mixture was emulsified using a vortex mixer for 2 minutes, leading to a stable emulsion of particle-coated water drops, whose sizes ranged from 100 to 1000 μm . We note that the negative charge of the PS particles interacts with the positively charged group of the RhB fluorescent dye, causing the dye to adhere on the surface of the particles. Therefore, only a fraction of the initial RhB concentration remains within the coated water drops, whose initial concentrations c_0 can be estimated *a posteriori* by computing the total amount of dye diffused from the drop.

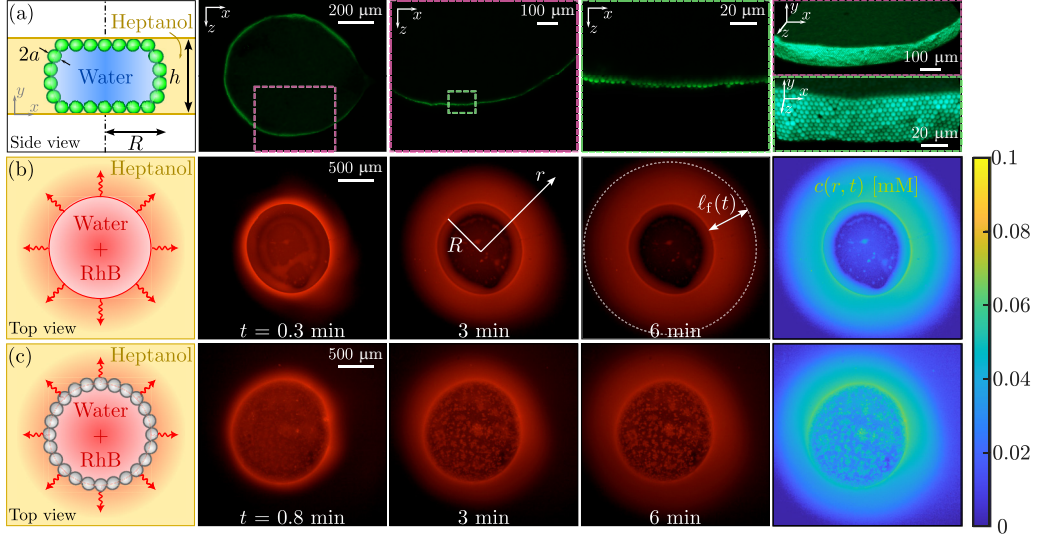


FIG. 1. Experimental snapshots of the diffusion from a drop with radius $R = 0.6$ mm. (a) Images of a drop coated with fluorescent polystyrene beads (radius $a = 2$ μm) obtained using confocal microscopy at different magnifications. The last panel illustrates the three-dimensional reconstruction of the particle coating. (b) The diffusion dynamics can be visualized using fluorescence microscopy by dissolving Rhodamine B (RhB) inside the drop. For a bare drop surrounded by heptanol, the dye diffuses radially outwards within minutes. The characteristic radial length scale quantifying the penetration depth is denoted as $\ell_r(t)$, which grows with time. (c) Coating the drop with polystyrene particles (radius $a = 5$ μm) still leads to the diffusion of RhB towards the outer phase. The image intensities can be converted to concentration fields $c(r, t)$ measured in [mM].

B. Confined two-dimensional drop geometry

To study the diffusion in a controlled manner, we isolate a particle-coated drop and confine it between two glass slides using an image spacer (Grace bio-Labs, Secure-Seal, radius 13 mm and thickness $h = 175$ μm). After the coated drop is deposited in the spacer, the spacer is filled with 1-Heptanol. A cover slip is then gently placed to cover the image spacer, squeezing the drop to a cylindrical pancake-like shape [Fig. 1(a)]. During the transfer of the coated drop, a small volume of hexadecane comparable to the drop volume, is carried into the heptanol bath. Because hexadecane and heptanol are fully miscible and have similar diffusivities, we do not expect the residual hexadecane to significantly affect the measured diffusion dynamics, as will be confirmed by the experimental results in Sec. III. The resulting two-dimensional droplet radius varies from $R = 0.40$ mm to 0.85 mm. The confined geometry allows for precise control of transport phenomena and has been successfully used to study droplet evaporation [32–35]. To systematically test the effect of the particle size, experiments were conducted for different particle sizes, with the particle radius $a = 0.05, 0.25, 0.50, 0.90, 2.50, 5.00$ μm spanning two orders of magnitude.

Squeezing the coated drop from a spherical geometry to a pancake-like shape can alter the morphology of the particle coating. To better understand how the change in geometry affects the coating morphology, we used confocal imaging to visualize the interfacial particles. To this end, we prepared dedicated Pickering emulsions stabilized by fluorescent polystyrene particles (Invitrogen, Thermo Fisher Scientific, $a = 2$ μm), from which a single drop was squeezed to a pancake shape. Figure 1(a) presents snapshots of the particle layer at different magnifications, showing the monolayer of particles at the interface between the drop and the surrounding liquid. The three-dimensional reconstruction of the coating confirms that the 2 μm particles form a monolayer, which does not get damaged during flattening of the drop. The close-up of the particle layer shows an hexagonal, close-packed configuration with sparse defects. From these images, the coverage fraction

is estimated to lie between $\phi_0 = 0.65$ and 0.75 . The addition of salt screens the electrostatic repulsion between the particles and may promote local aggregation during emulsifications, potentially leading to the formation of multilayers at the drop's interface. Optical and confocal microscopy show that multilayer regions are not formed for large particle sizes ($a = 0.90, 2.50, 5.00 \mu\text{m}$). For the smaller particles ($a = 50, 250, 500 \text{ nm}$), it was not possible to confirm the interfacial coverage and particle morphology.

C. Fluorescence microscopy

To visualize the diffusion process taking place in the two-dimensional cell we used a fluorescence microscopy setup. The RhB dye was excited with a wavelength of 540 nm , resulting in a fluorescent signal with emission wavelength of 625 nm , whose spatiotemporal evolution was recorded using a digital camera (DCC1645C, Thorlabs, frame rate of 0.1 fps) mounted on a microscope (Olympus BXFM, $2\times$ magnification). Typical snapshots of the diffusion process from a drop with radius $R = 0.6 \text{ mm}$ are shown in Figs. 1(b) and 1(c) for a bare drop and a coated drop with $a = 5 \mu\text{m}$, respectively. We point out that because diffusion occurs immediately once heptanol contacts the drop, the time delay caused by placing the cover slip prevents us from capturing the dynamics at the very early stages.

We chose water-heptanol-RhB for the multiphase-multicomponent system, as RhB emits a strong fluorescent signal in both liquids, which is vital to obtain accurate concentration measurements. In addition, RhB is soluble in both liquids and approximately 90 times more soluble in heptanol than in water. Specifically, the partition coefficient of RhB in water and heptanol was measured by bringing water-RhB solution in contact with a heptanol bath (1:1 v/v). After allowing the dye to equilibrate for 2 days, the partition coefficient was measured using a spectrophotometer (Hach Lange DR5000) and found to be $\kappa \equiv c_d/c_b = 1/88$, where c_d and c_b are the concentrations of the water drop and heptanol bath, respectively. The diffusivity of RhB in water has been measured previously to be $D_d \approx 4.2 \times 10^{-10} \text{ m}^2/\text{s}$ [36]. Using the Stokes-Einstein relation, we inferred the corresponding hydrodynamic radius of RhB and assumed that it remains unchanged in heptanol, yielding $D_d \approx 0.6 \times 10^{-10} \text{ m}^2/\text{s}$.

The captured image sequences were post-processed to obtain concentration fields. First, the raw images were converted to grayscale by extracting the intensity of the red channel $G(r, t)$, which varies with time t and radial position r from the center of the drop. The intensity in arbitrary units (a.u.) was converted to concentration values in [mM] by performing separate calibration experiments using known concentrations. The calibration was linear, such that the concentration field $c(r, t)$ can be computed as $c(r, t) = bG(r, t)$, with a calibration factor $b = 0.14 \text{ mM/a.u.}$ and $b = 0.18 \text{ mM/a.u.}$ for heptanol and water, respectively. The linear calibration fit remained valid provided that the normalized intensities did not exceed values of 70% that could arise from saturated images. Therefore, all of our experiments were conducted under the exact same illumination settings and exposure times to allow for the consistent conversion to concentration scales. Because the dye concentration $c(r, t)$ adopts a radially symmetric profile, we compute the radial dependence by taking the average along the circumference at every radial position r from the center of the drop. Because the drops are not always perfectly circular, the azimuthal averaging of the fluorescence intensity produces small discontinuities in the concentration profiles near the interface.

III. MEASUREMENTS OF CONCENTRATION FIELDS

The spatiotemporal evolution of the concentration field $c(r, t)$ is shown in Fig. 2, where it is plotted against the radial position r for different time instances. We start with an uncoated drop of radius $R = 0.6 \text{ mm}$ and initial RhB concentration $c_0 \approx 0.1 \text{ mM}$, corresponding to the snapshots shown in Fig. 1(b). During the early stages of diffusion the dye is still within the drop. The concentration profile is fairly flat near the center and sharply decreases close to the interface [Fig. 2(a)]. The jump in concentration expected from the favorable solubility of RhB towards

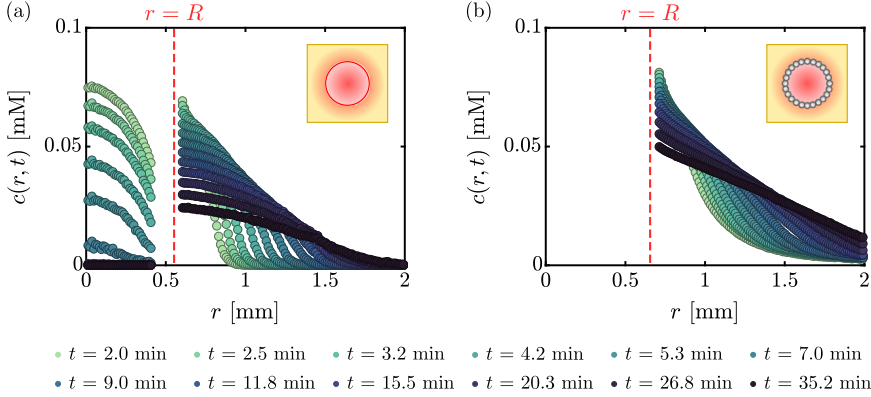


FIG. 2. Spatiotemporal evolution of the concentration field $c(r, t)$. (a) The concentration inside the bare drop decreases radially outwards. Crossing the interface, the favorable solubility of RhB towards heptanol causes a jump in the concentration, which then decreases radially. As time progresses, the concentration within the drop decreases and falls to zero once the drop has been depleted. Meanwhile, the concentration spreads radially outward in the heptanol bath. (b) Similar trends can be observed for the concentration field in heptanol generated by a coated drop with $a = 5 \mu\text{m}$.

heptanol can be clearly seen in the concentration profile as we cross the interface at $r = R$. As time progresses, the concentration profile spreads radially outward, while the interfacial concentration overall decreases. Similarly, the concentration within the drop decreases over time, maintaining the same spatial features of a radially decreasing profile. After approximately 7 minutes, the dye has diffused entirely into the outer phase.

We now switch to the concentration field generated by a coated drop with particle size $a = 5 \mu\text{m}$ [Fig. 2(b)]. The concentration within the drop is no longer accessible, as the particle coating prevents an accurate measurement of the spatial variation of the intensity. At each time instant, the concentration smoothly decreases in the radial direction, with the concentration gradient at the interface appearing to be sharper compared to the bare drop. As the dye penetrates into the bath, the interfacial concentration decreases over time. The overall trends of the spatiotemporal evolution of the concentration fields thus appear to be similar for the bare and coated drops. However, the concentration fields alone are insufficient to evaluate how the coating affects the diffusion dynamics.

One way to assess the influence of the particle coating is to quantify how far the dye penetrates into the bath. To this end, we compute the penetration length $\ell_f(t)$, labeled in Fig. 1(b), which is computed as the radial distance at which the normalized intensity G falls below 10%. The penetration length scaled by the drop radius R is plotted against the dimensionless time $D_b t / R^2$ [Fig. 3(a)]. We overlay the data for the different particle sizes a , which fall on top of that of a bare drop. Each data set follows a power law $\ell_f \sim (D_b t)^{1/2}$, often encountered in diffusive boundary layers, even in two-dimensional circular geometries [37]. Therefore, over a wide range of particle sizes, the coating does not affect the evolution of $\ell_f(t)$. Yet, even if the penetration depth remains unaltered by the presence of the particles, the amount of dye that has escaped the drop may be significantly reduced. We can thus reexamine the particle effects by investigating the time at which the total mass of the dye has diffused into the outer phase.

The total mass of diffused RhB in the outer phase $N_b(t)$ can be computed by integrating the experimentally measured concentration field in the heptanol phase as

$$N_b(t) = \int_R^\infty 2\pi r h c(r, t) dr. \quad (1)$$

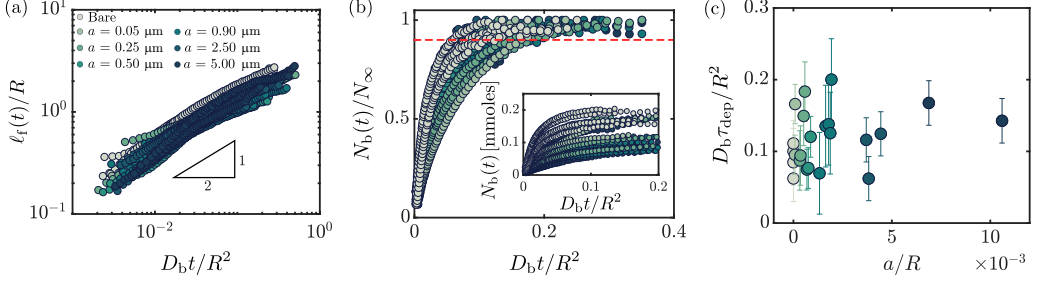


FIG. 3. Effect of particle size on the diffusion dynamics. (a) The scaled front length ℓ_f/R plotted against dimensionless time $D_b t/R^2$ for different particle radii a . The curves fall on top of each other, following the scaling $\ell_f \sim t^{1/2}$. (b) Amount of diffused material $N_b(t)$ normalized by its equilibrium value N_∞ against the dimensionless time $D_b t/R^2$. The collapse of the data suggests a negligible effect of the particles on how much dye diffuses into the bath. The red dashed line corresponds to when $N_b(t) = 0.9N_\infty$, which is used to compute the depletion time. Inset: The dimensional amount of diffused material in [mmol] plotted against the dimensionless time. (c) The normalized depletion time $\tau_{\text{dep}} D_b/R^2$ remains fairly constant with the normalized particle size a/R . The error bars are estimated by computing the depletion time as $N_b(t) = 0.95N_\infty$.

To avoid the small discontinuity in the azimuthally averaged concentration profile near the interface, the integration is performed starting at a radial position approximately 5% larger than the nominal drop radius. Plotting $N_b(t)$ against the dimensionless time $D_b t/R^2$, we observe a rapid increase at short times, before it plateaus to a constant equilibrium value N_∞ [Fig. 3(b) inset]. The equilibrium amount N_∞ varies between each experimental run, as it depends on the initial concentration c_0 inside the drop. Because the initial drop concentration is challenging to quantify for coated drops, we can assess the effects of the particles by measuring instead the time at which $N_b(t)$ plateaus. We thus compute the depletion time τ_{dep} by measuring the time at which the total mass $N_b(t)$ reaches 90% of N_∞ [dashed line in Fig. 3(b)]. Plotting the dimensionless depletion time $D_b \tau_{\text{dep}}/R^2$ against the particle size relative to the drop radius a/R , we find a variability in the data without any clear trend [Fig. 3(c)]. The scatter in the depletion time likely reflects the uncertainty associated with computing $N_b(t)$ from the measured concentration fields, which are subject to azimuthal averaging and small discontinuities near the interface. Nevertheless, since both the penetration length and depletion time do not exhibit any correlation with the particle coating, it is reasonable to conclude that their presence has a negligible effect on the diffusion dynamics.

IV. DIFFUSION ACROSS A PARTICLE-COATED INTERFACE

A. Model description

To better understand why the particles have minimal effect on the transport dynamics, we develop a one-dimensional diffusion model for a pancake drop with a particle-coated interface. We extend previous models on diffusion through a coated planar interface [30,31], which demonstrated that the particles only influence the dynamics at early times. We generalize this framework to a two-dimensional drop using a cylindrical coordinate system, with $r = 0$ defined at the center of the drop. The concentration field $c(r, t)$ is assumed to be axisymmetric and can be decomposed into a drop $c_d(r, t)$ and bulk $c_b(r, t)$ concentration [Fig. 4(a)]. The particle coating introduces a spatially varying area available for diffusion, which modifies the local transport rate across the interface. To account for this effect, we employ the Fick-Jacobs formalism, which provides an effective one-dimensional description of diffusion through a geometry with a spatially varying cross-sectional area [38,39]. The concentration fields therefore satisfy

$$\frac{\partial c_d}{\partial t} = \frac{D_d}{A(r)} \frac{1}{r} \frac{\partial}{\partial r} \left(r A(r) \frac{\partial c_d}{\partial r} \right) \quad \text{for } 0 < r < R \quad (2)$$

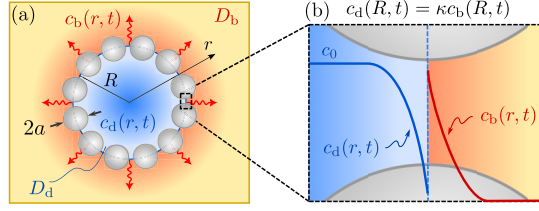


FIG. 4. (a) Schematic illustrating the diffusion from a drop with radius R and initial concentration c_0 . The drop has a concentration $c_d(r, t)$ and diffusivity D_d , while the surrounding bulk liquid has a concentration $c_b(r, t)$ and diffusivity D_b . (b) At the onset of diffusion, equilibrium partitioning at the interface relates the interfacial concentrations between the two phases, governed by the partition coefficient κ .

and

$$\frac{\partial c_b}{\partial t} = \frac{D_b}{A(r)} \frac{1}{r} \frac{\partial}{\partial r} \left(r A(r) \frac{\partial c_b}{\partial r} \right) \quad \text{for } R < r < \infty. \quad (3)$$

Here $A(r) = A_0[1 - \phi(r)]$ is the interfacial area available for diffusion, which depends on the uncoated area A_0 , and the particle surface coverage $\phi(r)$ that varies spatially across the layer. The classical Fick-Jacobs approximation is formally valid when the available cross-sectional area varies gradually. The present model incorporates diffusivity corrections [31,40,41], which account for the sharp variations near the particle edges.

Quantifying how the particles are arranged on the drop's interface is nontrivial, particularly when the spherically coated drop is squeezed into a disklike shape. Indeed, the curvature of the pancake drop limits the amount of spheres that can fit on the interface separating the two liquids. While the particles can be arranged on a planar interface with a well-defined surface coverage ϕ_0 , for a cylindrical drop the coverage becomes dependent on the ratio a/R . To minimize the complexity of our model, we relax this constraint and allow the particles to be arranged in lattices that are typically associated with planar interfaces. This quasi-1D model for the coating oversimplifies the particle arrangement on the interface, but should provide a fairly accurate description for $a/R \ll 1$. We thus proceed by assuming that the particles form a monolayer, whose surface coverage varies spatially as

$$\phi(r) = \begin{cases} \phi_0 \left[1 - \left(\frac{r-R}{a} \right)^2 \right] & \text{for } |r - R| \leq a, \\ 0 & \text{for } |r - R| > a. \end{cases} \quad (4)$$

To fully understand the effects of the surface coverage, we explore a wider range of ϕ_0 than accessed experimentally. We note that because we consider a two-dimensional cylindrical geometry, both the concentrations c_d and c_b , as well as the area $A(r)$, are expressed per arbitrary unit depth h .

The diffusion equations satisfy the regularity condition $\partial_r c_d|_{r=0} = 0$ at the center of the drop imposed by cylindrical symmetry, together with the far-field condition $c_b(\infty, t) = 0$. At the interface, equilibrium partitioning of the solute relates the drop and bulk concentrations $c_d(R, t) = \kappa c_b(R, t)$, as illustrated in Fig. 4(b). In addition, the continuity of the flux at the interface sets $D_d \partial_r c_d|_{r=R} = D_b \partial_r c_b|_{r=R}$. Finally, the initial condition for each concentration is $c_d(r, 0) = c_0$ and $c_b(r, 0) = 0$. We numerically solve Eqs. (2) and (3) using a centered finite difference scheme with logarithmically spaced grid points and time steps; see [31] for more details. We first nondimensionalize the radial distance r by the drop radius R and time t by the bulk's diffusive timescale R^2/D_b . The concentrations in the drop and the bulk are scaled by c_0 and c_0/κ respectively.

The nondimensionalization introduces four dimensionless parameters, reflecting the rich nature of the problem. These parameters can be separated into two groups: first, the mass transfer and thermodynamic properties give rise to the diffusivity ratio $\mathcal{D} = D_b/D_d$ and partition coefficient κ respectively. Second, the particle coating introduces the surface coverage ϕ_0 and particle size relative

to the drop radius $\epsilon = a/R$. From the numerical solution of the concentration field we compute the total mass as $N_b(t) = \int_R^\infty 2\pi r [1 - \phi(r)] c_b(r, t) dr$, which is then be used to assess the effects of the coating and transport properties on the depletion dynamics.

B. Bare drop analysis

To isolate the effects of the particle coating, it is instructive to first examine the effect of the transport parameters $\mathcal{D}$ and κ on the depletion of a bare drop. The interfacial area for a bare drop is constant $A(r) = A_0$, such that the Fick-Jacobs equations (2) and (3) reduce to the standard diffusion equations. This set of equations and boundary conditions does not admit any closed-form analytical solutions within the cylindrical framework adopted here. However, we can obtain analytical expressions if we treat the two phases as semi-infinite baths separated by a planar interface. We introduce the Cartesian coordinate $x = r - R$, such that the interface lies at $x = 0$, and neglect the curvature terms in (2) and (3). Replacing the regularity condition at $r = 0$ with $c_d(x \rightarrow -\infty, t) = c_0$, the concentration fields can be computed explicitly using the method of Laplace transforms, yielding [42]

$$c_d(x, t) = \frac{c_0}{1 + \sqrt{\mathcal{D}}/\kappa} \left[1 - \frac{\sqrt{\mathcal{D}}}{\kappa} \text{Erf}\left(\frac{x}{\sqrt{4\mathcal{D}t}}\right) \right] \quad \text{and} \quad c_b(x, t) = \frac{c_0}{\kappa(1 + \sqrt{\mathcal{D}}/\kappa)} \text{Erfc}\left(\frac{x}{\sqrt{4\mathcal{D}t}}\right). \quad (5)$$

These solutions for a planar interface are valid only for sufficiently early times. Importantly, however, they reveal the characteristic concentration scales at the interface $r = R$, which will be used to analyze the transport dynamics.

From the concentration fields we can compute the total mass diffused in the bulk. Rather than integrating over the available area, the total mass can also be computed by relating it to the interfacial flux $J|_{r=R} = -A_0 D_b c'_b|_{r=R}$ via the conservation of mass relation

$$\frac{dN_b}{dt} = -2\pi R D_b \left. \frac{\partial c_b}{\partial r} \right|_{r=R}. \quad (6)$$

Using the concentration field from (5), the total diffused mass for a planar interface becomes

$$N_{pl}(t) = \frac{2\pi R^2 c_0}{1 + \kappa/\sqrt{\mathcal{D}}} \left(\frac{4\mathcal{D}t}{\pi R^2} \right)^{1/2}. \quad (7)$$

To validate the planar approximation, we numerically solve the concentration fields using (2) and (3), from which we compute $N_b(t)$. We start by keeping a fixed partition coefficient $\kappa = 0.1$, while varying the diffusivity ratio $\mathcal{D}$. Figure 5(a) shows $N_b(t)$ normalized by its equilibrium value $N_\infty = \pi R^2 c_0$, plotted against time t scaled by the drop's diffusive timescale R^2/D_d . The numerical solutions for different values of $\mathcal{D}$ (solid lines) agree well with the planar solution (7) (dotted lines) at early times before they deviate and plateau at $N_b/N_\infty \rightarrow 1$, signaling the depletion of the drop. Yet the time required to reach equilibrium strongly depends on the transport properties. For low bulk diffusivities relative to the drop $\mathcal{D} \lesssim 1$, the curves collapse on top of each other, indicating an independence of the depletion dynamics on $\mathcal{D}$. Conversely, when the bulk diffusivity exceeds that of the drop $\mathcal{D} \gg 1$, the time taken to reach equilibrium significantly increases with $\mathcal{D}$.

To quantify the depletion dynamics we examine the effects of $\mathcal{D}$ and κ on the depletion time. Inspecting the mass balance (6), we see that depletion time scales as $\tau_{\text{dep}} \sim R c_0 / (D_b \partial_r c_b|_{r=R})$, which crucially depends on the interfacial concentration gradient. Thus, the remaining question is to determine how $\mathcal{D}$ and κ set the characteristic concentration and radial length scales in the bulk.

In the limit of low bulk diffusivities $\mathcal{D} \ll 1$, depletion typically occurs much faster than the diffusion in the bulk. Because of the low bulk diffusivity, the concentration develops over a length scale $\sqrt{D_b t} \ll R$, such that the planar solution (5) remains valid. Therefore, the characteristic interfacial concentration scales in the two phases become $c_d|_{r=R} \sim c_0/(1 + \sqrt{\mathcal{D}}/\kappa)$ and

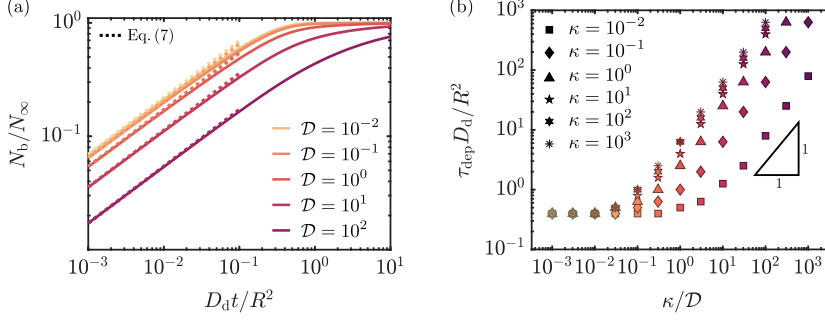


FIG. 5. Numerical results for the diffusion from a bare drop. (a) The numerical solutions (solid lines) of the normalized total mass per unit length N_b/N_∞ against the dimensionless time $D_d t/R^2$, for $\kappa = 0.1$ and different values of $\mathcal{D}$. At early times, each curve follows the planar solution (7) (dotted lines), before plateauing to its equilibrium value $N_\infty = \pi R^2 c_0$. The depletion time τ_{dep} is defined as the time at which N_b reaches 90% of N_∞ . (b) The dimensionless depletion time $\tau_{\text{dep}} D_d/R^2$ against the parameter $\kappa/\mathcal{D}$ for different values of κ (symbols). The depletion time remains constant for $\kappa/\mathcal{D} \ll 1$, while it increases linearly $\kappa/\mathcal{D}$ in the opposite limit.

$c_b|_{r=R} \sim (c_0/\kappa)/(1 + \sqrt{\mathcal{D}}/\kappa)$. Importantly, the two transport parameters combine in a single parameter in the form of $\sqrt{\mathcal{D}}/\kappa$. For $\kappa \ll \sqrt{\mathcal{D}} \ll 1$, the depletion is limited by the drop diffusivity, yielding a depletion timescale

$$\tau_{\text{dep}} \sim \frac{R^2}{D_d}. \quad (8)$$

Conversely, when $\sqrt{\mathcal{D}} \ll \kappa \ll 1$, the partitioning at the interface promotes the depletion as $c_b/c_0 \sim 1/\kappa \gg 1$. However, the low diffusivity of the bulk limits the diffusion, leading to a depletion timescale

$$\tau_{\text{dep}} \sim \kappa^2 \frac{R^2}{D_b} \sim \frac{\kappa^2 R^2}{\mathcal{D} D_d}, \quad (9)$$

which is amplified by a factor of $\kappa^2/\mathcal{D}$.

A different situation arises when $\kappa \gg 1$. In this limit, the bulk concentration becomes small $c_b/c_0 \sim 1/\kappa \ll 1$, while the interfacial concentration within the drop becomes comparable to c_0 . The resulting profile within the drop becomes uniform very fast, resembling the cases of bubble and drop dissolution [43,44]. Although the planar solution (5) remains valid at sufficiently early times, it no longer governs the depletion dynamics. Instead, depletion is controlled by the quasistatic concentration profile in the bulk. The dominant diffusion length scale therefore becomes R , and the characteristic concentrations must instead be obtained from the interfacial boundary conditions. This choice of length scale gives rise to the following scalings for the two concentration gradients $\partial_r c_b|_{r=R} \sim c_b|_{r=R}/R$ and $\partial_r c_d|_{r=R} \sim (c_0 - \kappa c_b|_{r=R})/R$, where in the latter we have used the partitioning at the interface. Combining these expressions with the interfacial flux boundary condition, the characteristic interfacial concentrations in each phase scale as $c_d|_{r=R} \sim c_0/(1 + \mathcal{D}/\kappa)$ and $c_b|_{r=R} \sim (c_0/\kappa)/(1 + \mathcal{D}/\kappa)$. The two transport properties now combine in a single parameter in the form of $\mathcal{D}/\kappa$. For $1 \ll \kappa \ll \mathcal{D}$, transport in the bulk is sufficiently fast that depletion is again limited by diffusion within the drop, yielding the timescale in (8). In contrast, when $\mathcal{D} \ll \kappa$, the poor solubility limits depletion, leading to

$$\tau_{\text{dep}} \sim \kappa \frac{R^2}{D_b} \sim \frac{\kappa R^2}{\mathcal{D} D_d}, \quad (10)$$

which is larger by a factor $\kappa/\mathcal{D}$.

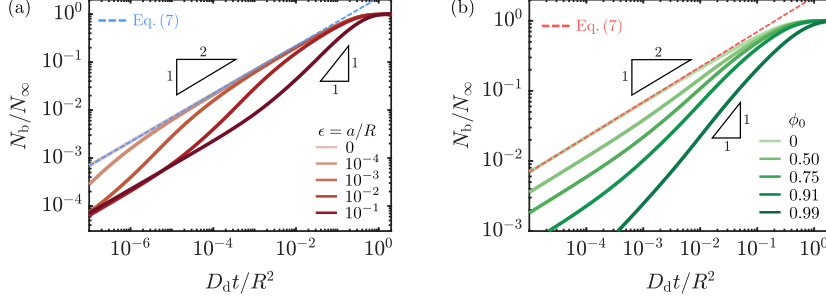


FIG. 6. Numerical results for the diffusion from a coated drop with $\mathcal{D} = 0.1$ and $\kappa = 0.01$. (a) The normalized total mass per unit length N_b/N_∞ against the dimensionless time $D_d t/R^2$ for a coated drop with $\phi_0 = 0.91$ and varying the relative particle size $\epsilon = a/R$. At early times, the bare drop follows the planar solution (7) (dotted line), while the coated drops are shifted downwards still following the $N_b \sim t^{1/2}$ scaling. (b) Keeping the particle size constant $\epsilon = 0.05$ and varying the coverage fraction, yields a similar behavior. Yet pushing the coverage to extreme values $\phi_0 = 0.99$ delays the depletion of the drop.

This scaling analysis reveals the emergence of three transport regimes, dictated by the relative values of $\mathcal{D}$ and κ .

(i) *Drop-limited depletion*, $\mathcal{D} \gg 1$ and $\mathcal{D} \gg \kappa$ or $\kappa \ll \sqrt{\mathcal{D}} \ll 1$: The high bulk diffusivity or relatively low partition coefficient promote the depletion towards the bulk, which is thus limited by the diffusivity in the drop. The characteristic timescale is given by (8).

(ii) *Bulk-limited depletion*, $\sqrt{\mathcal{D}} \ll \kappa \ll 1$: For low partition coefficients but relatively low bulk diffusivity the characteristic timescale is given by (9).

(iii) *Solubility-limited depletion*, $\mathcal{D} \ll \kappa$ and $\kappa \gg 1$: For a sufficiently high partition coefficient, the poor bulk solubility hinders diffusion and is characterized by (10).

To test these scaling predictions we again compute the depletion time τ_{dep} as the time when $N_b/N_\infty = 0.9$. Figure 5(b) shows the dimensionless depletion time $\tau_{\text{dep}} D_d/R^2$ against the parameter $\kappa/\mathcal{D}$. For low values of $\kappa/\mathcal{D}$ the depletion time scales as R^2/D_d , indicating the drop-limited regime, which is independent of the partition coefficient κ . In the opposite limit, the depletion time scales with $\kappa/\mathcal{D}$, lying in the solubility-limited regime. Yet the results for $\kappa \ll 1$ do not collapse on top of each other. While they still scale linearly with $\kappa/\mathcal{D}$ there is a dependence on the value of κ , as they lie within the third regime limited by the bulk's diffusivity.

C. Coated drop analysis

Having analyzed the effects of the transport properties, we now move on to study the diffusion of a coated drop. We begin by showing how the coating parameters ϵ and ϕ_0 affect the total mass, while keeping the transport properties constant at $\mathcal{D} = 0.1$ and $\kappa = 0.01$. Figure 6(a) shows the normalized total mass $N_b(t)/N_\infty$ diffused into the bulk against dimensionless time $D_d t/R^2$. We note that the equilibrium value N_∞ becomes slightly lower than $\pi R^2 c_0$ due to the volume occupied by the particles. For a fixed surface coverage $\phi_0 = 0.91$ and varying values of ϵ , we find that the curves for $N_b(t)$ deviate from the planar solution given by (7). At early times, the total mass still scales as $N_b \sim t^{1/2}$, but with a prefactor lower than the bare drop. Each curve undergoes a transition, where the total mass now appears to scale as $N_b \sim t$. The times at which these transitions occur increase with the particle size $\epsilon = a/R$. For sufficiently small particle sizes, the curves undergo another transition and fall on top of the planar solution. For large particle sizes equilibrium is reached before this second transition can take place and $N_b \rightarrow N_\infty$. Despite these differences, all curves reach the equilibrium value at approximately the same time.

We next examine the total mass, keeping $\epsilon = 0.05$ fixed and varying ϕ_0 [Fig. 6(b)]. At early times, the coating again causes the curves to fall below the solution of the bare drop. Each curve

follows the same $N_b \sim t^{1/2}$ scaling behavior, but with a prefactor that decreases with ϕ_0 . The coating again leads to a transition at early times; yet the linear growth $N_b \sim t$ becomes apparent only for large values of ϕ_0 . At later times, the curves fall on top of the bare solution, reaching the equilibrium value at the same time. Only when the surface coverage is increased to the extreme value $\phi_0 = 0.99$ does the depletion time increase roughly by a factor of two. Therefore, the particles appear to have a subtle role in the diffusion dynamics. The coating strongly affects the transport at early times, with the total mass undergoing a series of different temporal regimes. Yet the time it takes to fully deplete the drop remains unaffected, unless the surface coverage is increased to values beyond the close-packing limit.

Introducing the particle coating causes a decrease in the available area for diffusion compared to the bare drop. The interfacial now flux becomes $J|_{r=R} = A(R)D_b \partial_r c_b|_{r=R}$, leading to a mass balance

$$\frac{dN_b}{dt} = -2\pi R(1 - \phi_0)D_b \left. \frac{\partial c_b}{\partial r} \right|_{r=R}, \quad (11)$$

which differs from the bare drop relation (6) by a factor $1 - \phi_0$. The next step is to determine how the coating parameters affect the temporal evolution of the concentration gradient that gives rise to the different temporal regimes.

(i) *Early-time regime*: At very early times, the concentration profiles in both phases are situated around $r = R$ and the interfacial area becomes constant $A(R) = A_0(1 - \phi_0)$. Therefore, we can neglect the curvature and Fick-Jacobs terms in (2) and (3), leading to concentration fields described by the planar solution (5). The resulting interfacial concentration gradient becomes $\partial_r c_d|_{r=R} = c_0/[(\sqrt{D} + \kappa)\sqrt{\pi D_b t}]$, which when combined with (11), yields an exact expression for the total mass

$$N_b(t) = \frac{2\pi R^2 c_0(1 - \phi_0)}{1 + \kappa/\sqrt{D}} \left(\frac{4D_d t}{\pi R^2} \right)^{1/2}. \quad (12)$$

The total mass gets modified from bare planar solution (7) by a factor $1 - \phi_0$ and is independent of ϵ [31], confirming the numerical results observed in Figs. 6(a) and 6(b).

(ii) *Intermediate regime*: As the dye diffuses further within the particle layer, the increase in the available area becomes important. The radial term in the area profile becomes comparable to its baseline value $A_0(1 - \phi_0)$ over a length scale $a\sqrt{(1 - \phi_0)}$. For $t \gg a^2(1 - \phi_0)/D_b$, the concentration has developed past this region of the particle layer, such that no dye gets accumulated. As a result, the concentration field within $0 < r - R \lesssim a\sqrt{(1 - \phi_0)}$ can be treated as quasistatic with a spatially uniform flux. Performing a scaling analysis on the two interfacial boundary conditions combined with this radial length scale, leading to a concentration gradient as $\partial_r c_d|_{r=R} \sim c_0/[(D + \kappa)(a\sqrt{1 - \phi_0})]$. Using (11), the total mass adopts the scaling

$$N_b(t) \sim \frac{R^2 c_0}{(1 + \kappa/D)} \left(\frac{R\sqrt{1 - \phi_0}}{a} \right) \left(\frac{D_d t}{R^2} \right). \quad (13)$$

Unlike the early-time regime, the mass grows linearly with time, in agreement with the behavior observed in the first transition in Figs. 6(a) and 6(b).

(iii) *Late-time regime*: At late times the diffusion front has moved beyond the particle coating, leaving a flat concentration profile within the layer. Therefore, the concentration drops over a length scale in which there is no coverage, as $\phi(r) \rightarrow 0$ and $A(R) \rightarrow A_0$. The entire diffusion dynamics in this regime can be approximated via the bare-drop analysis, such that the concentration profiles are given by (5) and the total mass follows again the planar solution (7).

The times at which the transitions take place can be computed by comparing the expressions for the total mass between adjacent regimes. Equating (12) and (13), the duration for the early-time regime can be approximated as

$$\tau_{\text{early}} \sim \frac{\beta a^2(1 - \phi_0)}{D_d} \sim \epsilon^2(1 - \phi_0) \frac{\beta R^2}{D_d}, \quad (14)$$

where $\beta = [(1 + \kappa/\mathcal{D})/(1 + \kappa/\sqrt{\mathcal{D}})]^2$ is a parameter that depends on the transport properties. Thus, the transition towards the intermediate regime increases for larger particle sizes, as observed in Fig. 6(a). The timescale marking the end of the intermediate regime can be computed by comparing (13) and (7), leading to

$$\tau_{\text{int}} \sim \frac{\beta a^2}{D_d(1 - \phi_0)} \sim \frac{\epsilon^2}{(1 - \phi_0)} \frac{\beta R^2}{D_d}, \quad (15)$$

which diverges as $\phi_0 \rightarrow 1$.

With the exception of β , the timescales that define each regime adopt the same functional form as the planar interface [31]. Yet, as observed for large particle sizes or sufficiently covered interfaces, the late-time regime may never be reached, as the intermediate regime becomes so prolonged that the drop gets depleted before the transition can take place. In the extreme limit of $\phi_0 \rightarrow 1$, the intermediate regime becomes sufficiently large to delay the time required to deplete the drop. Therefore, a comparison between the depletion time of a bare drop and the duration of the intermediate regime provides a pathway to assess when the coating can hinder mass transport.

D. Criteria for transport hindrance

The coating will hinder mass transport as long as the duration of the intermediate regime given by (15) exceeds the depletion time set by the transport properties. When these criteria are met, the concentration gradient is controlled by the geometry of the particle layer in the intermediate regime. We can then reevaluate the depletion time by setting $t \sim \tau_{\text{dep}}$ and $N_b \sim R^2 c_0$ in (13). For drop-limited depletion, the particles will delay mass transfer when $\tau_{\text{int}} \gg R^2/D_d$. In this regime $\beta \sim 1$ as it is typically valid for $\mathcal{D} \gg \kappa$. Consequently, the depletion timescale follows

$$\tau_{\text{dep}} \sim \frac{\epsilon}{\sqrt{1 - \phi_0}} \left(\frac{R^2}{D_d} \right) \quad \text{for} \quad \frac{\epsilon}{\sqrt{1 - \phi_0}} \gtrsim 1, \quad (16)$$

which is larger than (8) by a factor $(\epsilon/\sqrt{1 - \phi_0})$. The solubility-limited regime is valid for $\kappa \gg \mathcal{D}$, such that $\beta \sim 1/\mathcal{D}$, yielding a depletion timescale

$$\tau_{\text{dep}} \sim \frac{\epsilon}{\sqrt{1 - \phi_0}} \left(\frac{\kappa}{\mathcal{D}} \frac{R^2}{D_d} \right) \quad \text{for} \quad \frac{\epsilon}{\sqrt{1 - \phi_0}} \gtrsim \sqrt{\kappa}. \quad (17)$$

This scaling expression is also larger from its bare drop value (10) by $(\epsilon/\sqrt{1 - \phi_0})$. Finally, for bulk-limited depletion $\sqrt{\mathcal{D}} \ll \kappa \ll 1$ occurs when $\epsilon/\sqrt{1 - \phi_0} \gtrsim \kappa$, but the depletion time still follows (17).

In all three cases the two particle properties combine to form a single dimensionless parameter $\epsilon/\sqrt{1 - \phi_0}$ that quantifies the coating effects. To test this modified behavior for the depletion time, we compute the depletion time over a wide range of values of ϵ , ϕ_0 , κ , and $\mathcal{D}$. Figure 7(a) shows the dimensionless depletion time $D_d \tau_{\text{dep}}/R^2$, against the coating parameter $\epsilon/\sqrt{1 - \phi_0}$. For constant values of $\kappa/\mathcal{D}$, the depletion time remains constant for $\epsilon/\sqrt{1 - \phi_0} \ll 1$, while in the opposite limit it scales linearly with $\epsilon/\sqrt{1 - \phi_0}$, confirming our scaling predictions. In addition, the transition at which the coating starts playing a role depends on the value of κ .

To place our experimental results within this context, we overlay the average of our experimentally computed depletion times of Fig. 3(c). The experimental data are consistent with the scaling predictions and lie in the regime where the particles have essentially no effect on the depletion time. The fact that the experiments cover only a narrow range of the coating parameter $\epsilon/\sqrt{1 - \phi_0}$, reflects the limited range of surface coverages accessible with the model system used in our experiments, which was selected to systematically vary the particle size, and to obtain a controlled monolayer morphology for comparison with the theoretical predictions. The remaining portion of the numerical results corresponds to interfaces with substantially higher surface coverages, which may be experimentally achieved through postprocessing strategies such as thermal [28] or chemical

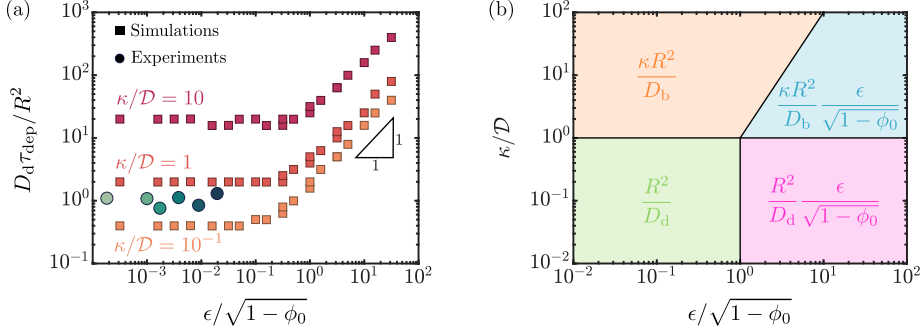


FIG. 7. Phase plots for the depletion dynamics of coated drops. (a) Plotting scaled depletion time $\tau_{dep} R^2 / D_d$ against the coating parameter $\epsilon / \sqrt{1 - \phi_0}$, two limiting behaviors emerge for constant values of κ / D . For low values of $\epsilon / \sqrt{1 - \phi_0}$, the depletion time remains constant; yet, for large values of $\epsilon / \sqrt{1 - \phi_0}$, the depletion time scales linearly with $\epsilon / \sqrt{1 - \phi_0}$. The colors of the experimental symbols (circles) correspond to the different particle sizes investigated experimentally and are the average values of the data shown in Fig. 3(c). (b) Phase diagram showing the different asymptotic cases for the depletion time as a function of the coating and transport properties. On the horizontal axis the coating properties quantified by the parameter $\epsilon / \sqrt{1 - \phi_0}$, while on the vertical axis the transport properties are quantified by the parameter κ / D .

[29] sintering of the particle layer. Such systems are expected to lie on the right-hand side of Fig. 7(a), where the particle coating prolongs the depletion time.

To combine all the different cases that characterize the depletion dynamics of a coated drop, we present the asymptotic limits in a phase diagram in Fig. 7(b). The horizontal axis indicates the coating properties, which can be quantified by the dimensionless parameter $\epsilon / \sqrt{1 - \phi_0}$. Similarly, the transport and thermodynamic properties can also be grouped into the parameter κ / D , which is used as the vertical axis. For $\kappa / D < 1$, transport is limited by the drop's diffusivity, becoming further restricted by the particle coating when $\epsilon / \sqrt{1 - \phi_0} > 1$. For $\kappa / D > 1$, the depletion is now governed by the bulk solubility, with the particles further prolonging depletion when $\epsilon / \sqrt{1 - \phi_0} > \sqrt{\kappa}$. We note that the present phase does not account for the regime limited by the bulk's diffusivity, as κ and D govern the transport dynamics separately.

V. CONCLUSION AND OUTLOOK

We have investigated how particles adhered to interfaces affect interfacial diffusion from two-dimensional drops. Using fluorescent microscopy experiments, we characterized the concentration fields for diffusion from drops coated with a monolayer of spherical particles, whose size was varied by almost two orders of magnitude. We demonstrated that the particles have a minimal effect on the transport dynamics, as quantified by the penetration length and depletion time. These results were rationalized by a one-dimensional diffusion model consisting of a particle-coated interface. The model revealed that the presence of particles induced three temporal transport regimes, each governed by the local concentration gradient within the layer. A comparison between the particle-dominated regime and the depletion time of the drop indicated when the coating delays mass transport, consistent with our experimental observations.

Our theoretical analysis provide a framework to predict when the particle coating influence mass transport [Fig. 7(b)]. In practice, the surface coverage ϕ_0 is the dominant parameter governing transport, given that $\epsilon = a/R$ is typically limited to values below ~ 0.1 . For a monolayer of spherical particles, as in our experiments, the highest attainable coverage corresponds to hexagonal close packing $\phi_0 = 0.91$, which is insufficient to strongly affect the interfacial flux. Particle monolayers can hinder transport if the surface coverage is increased beyond this limit [31], for instance, via particle sintering [28,29]. For extreme values of surface coverage, or if the solute is a macro-

molecule, the pore size can become comparable to, or smaller than the solute size. In this case our continuum framework no longer applies, and steric confinement is expected to introduce an additional transport resistance. Such effects are particularly relevant for encapsulation or controlled release of macromolecules, for instance enzymes [45] and polysaccharides [46]. Multilayers of particles are also hypothesized to hinder diffusive transport [24,47] although the effect has not yet been characterized quantitatively and has been prevented as much as possible in our experiments. While the model presented here can be extended to describe multilayers of particles, provided that the layer morphology is known, in future work it can be interesting to describe more complex layers with an effective diffusivity.

More broadly, these results clarify how particle-coated interfaces regulate mass transfer in Pickering emulsions used in food products [48,49], controlled release [17], and multiphase chemical conversion [50]. In these systems, particle layers are often assumed to significantly hinder transport; yet, our results show that their effects on transport remains weak in practical settings. This behavior is specific to discrete microscopic particle coatings, where transport occurs through pores formed between adjacent particles, and differs from surfactant or lipid layers, where interfacial transport is governed by mechanisms on the molecular scale. Bridging these length scales may provide a unified framework to understand how interfacial coatings govern mass transfer.

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DATA AVAILABILITY

The data that support the findings of this article are openly available [51].

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