

# Assignment 1 Transport phenomena

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## Abstract

This study investigates surfactant transport on the surface of a small spherical gas bubble rising in a quiescent, isothermal Newtonian liquid. The objective is to determine the steady surface concentration  $\Gamma(\theta)$  of an insoluble surfactant (with  $\bar{\Gamma}$  denoting its mean value) and to quantify how interfacial advection and surface diffusion set its distribution. Under creeping-flow and axisymmetric conditions, the interfacial balance reduces to the steady surface advection-diffusion equation on the bubble surface. Nondimensionalization with the bubble radius  $R$  and a characteristic surface speed  $U_s$  introduces the surface Péclet number ( $Pe_s = \frac{U_s R}{D_s}$ ). With an axisymmetric tangential interfacial kinematics, the equation integrates into a first-order differential equation.

$$\boxed{\Gamma(\theta) = \bar{\Gamma} \frac{k}{\sinh(k)} e^{-k \cos(\theta)}}$$

This closed-form distribution  $\Gamma(\theta)$  satisfies pole regularity and global mass conservation. The results show that as  $k \rightarrow 0$ , the system is dominated by diffusion with an "immobile" interface. However, increasing  $k$  produces a front-rear asymmetry in the system, characteristic of Marangoni retardation.

## Nomenclature

$\mu$	Dynamic viscosity [kg/(m·s)].
$p$	Pressure [Pa].
$\hat{p}$	Gas pressure inside the bubble [Pa].
$\mathbf{v}$	Velocity [m/s].
$\Gamma$	Surface concentration [ $\text{mol} \cdot \text{m}^{-2}$ ].
$\bar{\Gamma}$	Average surface concentration [ $\text{mol} \cdot \text{m}^{-2}$ ].
$\gamma(\Gamma)$	Surface tension [N/m].
$D_s$	Surface diffusivity [ $\text{m}^2/\text{s}$ ].
$R$	Bubble radius [m].
$U$	Bubble rising velocity [m/s].
$a$	Degree of surface interface mobility.
$k$	Mobility advection parameter [-]
(RHS)	Right-hand side of an equation.
(LHS)	Left-hand side of an equation.

## Geometry & operators

$S$  Gas-liquid interface (bubble surface).

$\theta, \phi$  Polar and azimuthal angles.

$n$  Unit normal on  $S$ , taken out of the bubble and into the liquid.

$t$  Unit tangent (any orthonormal basis on the tangent plane of  $S$ ).

$\nabla_s$  Surface (interfacial) gradient operator.

$\nabla_s \cdot$  Surface divergence operator

## Dimensionless groups

- Péclet number  $\Rightarrow \frac{U_s R}{D_s}$
- Reynolds number  $\Rightarrow = \frac{\rho U R}{\mu}$
- Capillary number  $\Rightarrow \frac{\mu U}{\gamma}$

## 1. Introduction

Gas bubbles rising in liquids are fundamental to many natural and industrial processes, such as wastewater treatment, fermentation, aeration and chemical process engineering. Their motion and interfacial behavior are strongly influenced by the presence of surface-active agents (surfactants). Even at very low concentrations, surfactants can adsorb at the gas-liquid interface and create gradients in surface tension. These gradients give rise to Marangoni stresses, which oppose the flow along the bubble's surface, significantly impacting its mobility, shape and the rates of heat and mass transfer across the interface. Consequently, the same bubble can behave like a clean, free-slip sphere or a rigid, no-slip particle, depending entirely on the transport of surfactants at its interface.

## Governing physical phenomena

The complex behavior of a surfactant-laden bubble is dictated by a dynamic interplay of multiple physical phenomena. The primary phenomena at play are:

**Buoyancy:** The bubble's motion is governed by a balance between the upward buoyancy force, driven by the density difference with the surrounding liquid.

**Viscous drag:** The retarding force exerted by the liquid that opposes the bubble's upward motion.

**Surfactant transport:** Since the surfactant is confined to the interface, its movement is governed by two key mechanisms:

- Surface advection: Surfactant is carried along by the tangential flow of the liquid at the bubble's surface.
- Surface diffusion: Surfactant molecules move from regions of high concentration to low concentration, a process that counters the effects of advection.

## Objectives and report structure

The aim of this work is to analyze the interfacial transport of surfactant and its surface concentration  $\Gamma(\theta)$ , influenced by the change of different parameters.

The study follows a systematic approach: (1) identification of the dominant physical phenomena, (2) formulation of governing equations and boundary conditions, (3) non-dimensionalization and scaling analysis, (4) solution of the simplified model, and (5) a parameter study of the most relevant quantities.

## 2. Assumptions & boundary conditions

To simplify the analysis and render the surfactant transport problem tractable, the following physical model assumptions were added. These ensure that the interfacial balance reduces to a steady surface equation on the bubble interface, complemented by appropriate boundary/regularity and mass-conservation constraints.

### Physical setup

The problem considered here consists of a single gas bubble of radius  $R$  rising steadily in a quiescent, isothermal Newtonian liquid. The primary aim is to determine the steady surface concentration  $\Gamma(\theta)$  on the bubble's gas–liquid interface  $S$ .

### Key assumptions

1. The bubble achieves its terminal (steady) rise speed  $U$ , so its velocity is constant in time.
2. The bubble remains spherical (i.e. its shape does not deform), under the assumption that surface tension dominates over gravitational and hydrodynamic distortions. This is guaranteed when the Capillary number is small ( $Ca \ll 1$ ).
3. The surfactant is effectively insoluble over the timescales of interest: no exchange occurs with the bulk fluid (source term  $s = 0$ ). All surfactant resides on the interface.
4. The interface is impermeable (no normal velocity through it), so

$$v \cdot n = 0 \quad \text{on } S,$$

and only tangential transport contributes to interfacial redistribution.

5. The problem is axisymmetric and steady: variables such as  $\Gamma$  depend solely on the polar angle  $\theta$ , not on the azimuthal angle  $\phi$ .
6. The flow regime is in the creeping (Stokes) limit, i.e. the Reynolds number is small,

$$\text{Re} = \frac{\rho U R}{\mu} \ll 1.$$

Under this assumption, inertia is negligible compared to viscous forces and the Navier–Stokes equations reduce to the steady Stokes equations. Consequently, on the interface only tangential advection and surface diffusion remain in the transport balance.

7. Since the flow is axisymmetric and in the Stokes limit, the tangential velocity will be assumed to take the form of  $u_\theta = a \cdot \sin(\theta)$ , where  $a$  is a constant related to the degree of interface mobility.

### Hypotheses and predictions

Given the assumptions taken into consideration, the following possible outcomes were hypothesized:

- **H1** (diffusion-dominated): When interfacial advection is weak relative to surface diffusion (small surface Péclet number  $P_{es}$ ),  $\Gamma(\Theta)$  is nearly uniform over the interface.

- **H2** (advection-dominated trend): As interfacial advection strengthens (larger  $P_{es}$ ),  $\Gamma(\theta)$  develops a front-back asymmetry, with accumulation toward the rear pole of the rising bubble and depletion near the front.
- **H3** (immobilized limit): If the interface is effectively immobile (no tangential motion along the surface), the steady distribution returns to uniform  $\Gamma$  irrespective of  $P_{es}$

### 3. Mathematical formulation

#### Interfacial transport balance

The standard conservation law for an insoluble species confined to a moving interface  $S$  reads

$$\underbrace{\partial_t \Gamma}_{\text{unsteady}} + \underbrace{\nabla_s \cdot (\Gamma \mathbf{v}_s)}_{\text{tangential advection}} + \underbrace{\Gamma (\nabla_s \cdot \mathbf{n}) v_n}_{\text{area change}} = \underbrace{\nabla_s \cdot (D_s \nabla_s \Gamma)}_{\text{surface diffusion}} + \underbrace{s}_{\text{ads./des.}} \quad (1)$$

With the assumptions from chapter 2, (steady, insoluble  $s = 0$ , fixed sphere radius  $v_n = 0$ ), this reduces the equation to the steady surface advection-diffusion balance equation

$$\boxed{\nabla_s \cdot (\Gamma v_{ts}) = D_s \nabla_s^2 \Gamma} \quad (2)$$

### 4. Scaling and nondimensionalization

This chapter introduces scales and nondimensional variables that reduce the interfacial transport problem to a parameter-minimal form, identify the controlling groups, and prepare the equation for analysis on a unit sphere.

The bubble radius ( $R$ ) is used as the length scale and a characteristic tangential interfacial speed  $v_{ts}$  as the surface-velocity scale. The surface concentration is scaled by a reference value  $\Gamma_{ref}$ .

$$x^* = \frac{x}{R}, \quad v_{ts}^* = \frac{v_{ts}}{U_s}, \quad \Gamma^* = \frac{\Gamma}{\Gamma_{ref}}, \quad \nabla_s = \frac{1}{R} \nabla_s^*$$

With all the equations presented and substituting into (2);

$$(\text{LHS}) \nabla_s \cdot (\Gamma v_{ts}) = \frac{1}{R} \nabla_s^* \cdot (\Gamma_{ref} \Gamma^* U_s v_{ts}^*)$$

$$(\text{LHS}) \nabla_s \cdot (\Gamma v_{ts}) = \frac{\Gamma_{ref} U_s}{R} \nabla_s^* \cdot \Gamma^* v_{ts}^*$$

$$(\text{RHS}) D_s \nabla_s^2 \Gamma = \frac{\Gamma_{ref} D_s}{R^2} (\nabla_s^*)^2 \Gamma^*$$

Dividing both sides by  $\frac{\Gamma_{ref} D_s}{R^2}$  and dropping the asterisks:

$$\nabla_s^2 \Gamma = P_{es} \nabla_s \cdot (\Gamma v_{ts}) \quad (3)$$

For any axisymmetric scalar  $\Gamma(\theta)$  and tangential velocity  $v_{ts} = u_\theta e_\theta$ :

$$(\text{LHS}) \nabla_s^2 \cdot \Gamma = \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Gamma}{d\theta} \right) \quad (\text{Unit sphere})$$

$$(\text{RHS}) \nabla_s \cdot (\Gamma v_{ts}) = \frac{1}{\sin \theta} \frac{d}{d\theta} (\sin \theta \Gamma u_\theta(\theta))$$

Ending up as:

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Gamma}{d\theta} \right) = P_{es} \frac{1}{\sin \theta} \frac{d}{d\theta} (\sin \theta \Gamma u_\theta(\theta)) \quad (4)$$

Integrating (4) once gives;

$$\sin(\theta) \frac{d\Gamma}{d\theta} - P_{es} \sin(\theta) \Gamma u_\theta(\theta) = C$$

Applying the pole-regularity condition, further described in 6, but which requires that  $\sin(\theta) \frac{d\Gamma}{d\theta} \rightarrow 0$  and  $\sin(\theta) \Gamma u_\theta(\theta) \rightarrow 0$  for  $\theta = 0, \pi$ . With these conditions, the integration constant is zero, yielding the following first-order ODE.

$$\frac{d\Gamma}{d\theta} = P_{es} \Gamma u_\theta(\theta) + \mathcal{C}^0 \quad (5)$$

Separating the variables in the differential equation:

$$\frac{d\Gamma}{\Gamma} = P_{es} u_\theta(\theta) d\theta \Rightarrow \Gamma(\theta) = C \exp \left( (P_{es} \int_0^\theta u_\theta(\eta) d\eta) \right)$$

Using  $u_\theta = a \cdot \sin(\theta)$ , its integral is:

$$\int_0^\theta u_\theta(\eta) d\eta = -a \cos(\theta) + a \Rightarrow \Gamma(\theta) = C e^{(-a P_{es} \cos(\theta))} \quad (6)$$

Now, the value of the constant  $C$  is calculated by enforcing the mass conservation of the system  $\int_0^\pi \Gamma(\theta) \sin(\theta) d\theta = 2\bar{\Gamma}$ :

$$\int_0^\pi C e^{-a P_{es} \cos(\theta)} \sin(\theta) d\theta = \frac{C}{a P_{es}} (e^{a P_{es}} - e^{-a P_{es}})$$

Letting  $k = a P_{es}$  and using the sinh simplification:

$$\frac{2}{k} \sinh(k) \cdot C = 2\bar{\Gamma} \Rightarrow C = \bar{\Gamma} \frac{k}{\sinh(k)}$$

The final formula, isolating the surface concentration, ends up as:

$$\boxed{\Gamma(\theta) = \bar{\Gamma} \frac{k}{\sinh(k)} e^{-k \cos(\theta)}} \quad (7)$$

## 5. Analytical solution

This section develops the governing relations for surfactant transport and interfacial stresses.

Starting from the calculated concentration distribution (7), the balance of viscous, capillary, and Marangoni forces is analyzed. The nondimensional groups ( $Re$ ,  $Ca$ ,  $Pe$ ,  $Ma$ ) are used to interpret the bubble dynamics under given conditions.

### Validation of governing regime

Before analyzing the surfactant concentration distribution, it is crucial to validate the assumptions made to simplify the governing equations. The model relies on a number of key assumptions, including negligible inertia and a spherical bubble shape, which are valid only within specific physical regimes.

This section uses certain fluid and bubble parameters to calculate the relevant dimensionless groups—the Reynolds, Capillary, and Marangoni numbers—to confirm that our chosen physical model accurately describes the system.

The following parameters are used in these calculations; bubble radius:  $R = 1.0 \times 10^{-5}$  m, fluid of density:  $\rho = 1000$  kg/m<sup>3</sup>, fluid viscosity:  $\mu = 0.001$  Pas, surface tension:  $\gamma_0 = 0.072$  N/m, gravitational acceleration:  $g = 9.81$  m/s<sup>2</sup>, diffusion coefficient:  $D_s = 1 \times 10^{-9}$  m<sup>2</sup>/s, average concentration:  $\bar{\Gamma} = 2.0 \times 10^{-6}$ , mol/m<sup>2</sup> surface elasticity:  $E = 0.03$  N·m/mol, rising speed:  $U = 0.300$  mm/s =  $3.0 \times 10^{-4}$  m/s.

#### 1. Reynolds number ( $Re$ )

The assumption model used  $Re \ll 1$ .

$$Re = \frac{\rho U R}{\mu} = \frac{(1000)(0.0003)(0.00001)}{0.001}$$

*Interpretation:*  $Re = 0.003$ . While not deep into the  $Re \ll 1$  regime, the inertial terms are negligible, and the creeping flow (Stokes) assumption is strongly validated.

#### 2. Capillary Number ( $Ca$ )

Measures the ratio of viscous forces to surface tension forces. The model used  $Ca \ll 1$  to keep the spherical shape.

$$Ca = \frac{\mu U}{\gamma_0} = \frac{(0.001)(0.0003)}{0.072}$$

*Interpretation:*  $Ca \approx 4.17 \times 10^{-6}$ . This is very small, confirming the assumption that viscous stresses are too weak to deform the bubble against the strong surface tension.

#### 3. Marangoni Number ( $Ma$ )

The Marangoni number quantifies the relative importance of Marangoni stresses (surface tension gradients) to viscous stresses, driving the transition between the clean and rigid limits.

$$Ma = \frac{E \bar{\Gamma}}{\mu U} = \frac{(0.03)(2 \times 10^{-6})}{(0.001)(0.0003)} = 0.2$$

*Interpretation:* The fact that  $Ma$  is of order  $\mathcal{O}(1)$  (i.e not  $\ll 1$ ) confirms that Marangoni stresses are significant and cannot be ignored. They are comparable in magnitude to the viscous stresses exerted by the liquid flow

### Parameter study and outcomes

The system's behavior is primarily governed by the advection-diffusion balance, quantified by the parameter

$$k = a Pe_s.$$

The Surface Péclet number  $Pe_s$  captures the scale of the flow relative to diffusion and the constant  $a$  represents the influence of interfacial mobility on the tangential flow

This value of  $a$  links the concentration profile  $\Gamma(\theta)$  to the physical state of the interface and is bounded by two well-known limits in the creeping flow regime:

- Clean Interface (Free-slip limit): When the surfactant effect is negligible, the interface is fully mobile. The flow is described by the Hadamard-Rybczynski solution, giving the maximum value for  $a$ :  $a = \frac{3}{2}U$ .
- Rigid Interface (Immobilized limit): When the Marangoni stresses are sufficient to fully stop the tangential flow, the interface behaves like a no-slip wall. In this case, the mobility constant is zero:  $a = 0$ .

### Study 1: Surfactant concentration at different raising velocities ( $U$ )

Study 1 investigates the dimensional surface concentration  $\Gamma(\theta)$  as a function of the bubble's rising velocity  $U$  while keeping other parameters fixed. This directly examines the influence of the advective scale on the surfactant distribution. The results for various rise speeds are visually presented in fig.1, with the physical transitions explained below:

- At very low rise speeds ( $U = 1 \times 10^{-5}$  m/s), advection is weak. The concentration  $\Gamma(\theta)$  is

nearly uniform, showing diffusion-dominated transport.

- For moderate speeds ( $U = 3 \times 10^{-4}$  m/s), advection starts to sweep surfactant from the front ( $\theta = 0$ ) to the rear ( $\theta = 180$ ). The concentration develops a gentle front-rear asymmetry, with accumulation becoming noticeable at the rear pole.
- At higher speed such as ( $U = 1 \times 10^{-3}$  m/s) & ( $U = 1 \times 10^{-2}$  m/s), advection strongly dominates surface diffusion ( $k \gg 1$ ). The profile becomes severely asymmetric, showing near-total depletion at the front and significant enrichment at the rear.

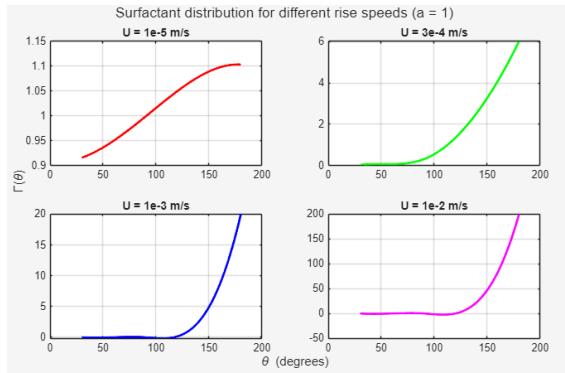


Figure 1. Normalized  $\frac{\Gamma(\theta)}{\bar{\Gamma}}$  for different rising velocities using eq. (7).

### Study 2: $\Gamma(\theta)$ vs. Polar angle $\theta$ & $k$

The computational results are presented in Figure 2, followed by their interpretation.

- At low  $k$ , surface diffusion smooths out the effect of the tangential flow, so the surface concentration remains close to uniform. The profile shows only a gentle front-rear asymmetry.
- At high  $k$ , advection along the interface outweighs diffusion and transports surfactant toward the rear. The profile becomes strongly asymmetric, having a pronounced depletion form at the front while a distinct accumulation “cap” develops around the rear of the bubble. Gradients steepen and concentrate in a narrower zone separating the depleted front from the enriched rear, producing a visibly sharper transition compared with the small- $k$  case. Further mathematical analysis can be found in the Appendix (6).

Since  $k$  is directly proportional to the rise speed  $U$  (as  $k \propto aU$ ), varying  $U$  (Study 1) has the same physical effect on the  $\Gamma(\theta)$  profile as varying the

non-dimensional parameter  $k$  (Study 2), as they both capture the strength of advective transport.

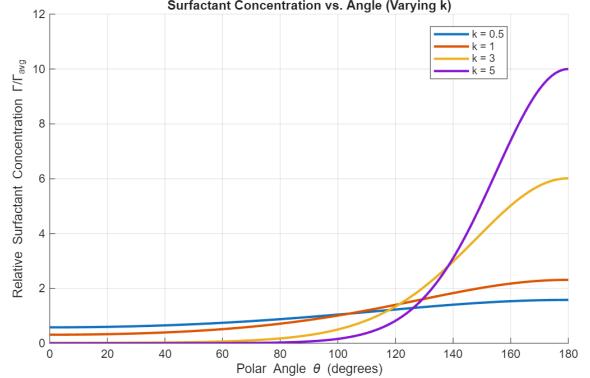


Figure 2. Normalized surface concentration distribution for different  $k$  values following curve from (7).

## Study 1 & 2 conclusions

The Surface Péclet number ( $Pe_s$ ) serves as the critical non-dimensional parameter governing the transport of insoluble surfactant for the derived formula (7). The value of  $Pe_s$  dictates the nature of the steady-state concentration profile  $\Gamma(\theta)$ :

As  $Pe_s \rightarrow 0$  (or  $k \rightarrow 0$ ), transport is dominated by surface diffusion. This results in a nearly uniform concentration  $\Gamma(\theta) \approx \bar{\Gamma}$  across the bubble surface.

As  $Pe_s$  increases (or  $k$  increases), transport becomes dominated by surface advection. The tangential flow vigorously sweeps surfactant molecules from the front stagnation point ( $\theta = 0^\circ$ ) toward the rear stagnation point ( $\theta = 180^\circ$ ) faster than diffusion can redistribute them. This creates a pronounced front-rear asymmetry, marked by surfactant depletion at the front and significant accumulation at the rear. This steep concentration gradient generates large Marangoni stresses, which physically retard the flow and reduce the overall rise speed of the bubble.

In the system analyzed, where  $Pe_s$  is often  $O(1)$  or greater, the resulting asymmetry confirms the necessity of the full advection-diffusion model and highlights the critical influence of surfactants on bubble dynamics.

## 6. Conclusion

This project successfully investigated the steady-state surface concentration  $\Gamma(\theta)$  of an insoluble surfactant on a small, spherical gas bubble rising in a quiescent liquid under the creeping-flow regime ( $Re \ll 1$ ). By simplifying the full interfacial transport balance to a steady surface

advection-diffusion equation, the surface concentration was derived as a function of the mobility-advection parameter,  $k$ :

$$\Gamma(\theta) = \bar{\Gamma} \frac{k}{\sinh(k)} e^{-k \cos(\theta)}$$

The dimensional analysis confirmed that the chosen physical model was appropriate for the parameters used, operating in a low-deformation, inertia-negligible regime ( $Ca \ll 1$  and  $Re \ll 1$ ).

## Confirmation of hypothesis

The parameter studies (varying  $U$  and  $k$ ) validated the initial hypotheses:

- **Hypothesis H1:** Confirmed.

As  $k \rightarrow 0$  (low rise speed  $U$ ), surface diffusion dominates, leading to a nearly uniform concentration profile  $\Gamma(\theta) \approx \Gamma_0$ .

- **Hypothesis H2 :** Confirmed.

As  $k$  increases (high rise speed  $U$ ), advection sweeps the surfactant, causing a pronounced front-rear asymmetry marked by depletion at the front ( $\theta = 0^\circ$ ) and accumulation at the rear ( $\theta = 180^\circ$ ).

- **Hypothesis H3:** Confirmed implicitly.

The immobilized limit ( $a = 0$ ) results in  $k = 0$ , which naturally returns the system to the diffusion-dominated uniform concentration, irrespective of the fluid flow rate.

The primary physical outcome of the analysis is that the transport of surfactant on the interface determines the bubble's effective mobility. The steep concentration gradients created at high  $k$  generate large Marangoni stresses. These surface-tension gradients oppose the tangential flow, physically retarding the bubble's ascent and forcing the interface to transition toward the behavior of a rigid, no-slip particle. Understanding this transition is essential for predicting heat and mass transfer rates in industrial and natural processes involving bubbles.

## Model limitations and Potential outcomes

The analytical solution's simplicity is dependent on several strict assumptions. If certain assumptions were relaxed, the problem complexity and physical outcomes would change significantly:

- Finite Reynolds number ( $Re \sim 1$ ): Relaxing the creeping flow assumption ( $Re \ll 1$ ) would necessitate solving the full Navier-Stokes equations. This would introduce inertial effects into the fluid flow, which would modify the velocity profile  $u_\theta$  and likely lead to a more complex, non-analytical solution for  $\Gamma(\theta)$ .

- Soluble surfactant ( $s \neq 0$ ): Relaxing the insoluble surfactant assumption (source term) would introduce the adsorption/desorption of surfactant between the interface and the bulk liquid. This introduces a new time scale and dependency on the bulk concentration ( $C$ ), making the interfacial concentration  $\Gamma(\theta)$  dependent on the kinetic rate constants rather than just advection and diffusion.

- Deformable bubble shape ( $Ca \sim 1$ ): Relaxing the spherical shape assumption ( $Ca \ll 1$ ) would require coupling the interfacial transport equation with the hydrodynamic equations that govern the bubble's shape. The resulting surface velocity profile  $v_{ts}$  would be non-analytical, and the concentration distribution would further influence the shape via Marangoni stresses (a coupled, non-linear problem).

This mobility transition is directly relevant to applications such as aeration, fermentation, and wastewater treatment, where interfacial contamination controls bubble-driven mass and heat transfer.

## References

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- [2] H. A. Stone. “A simple derivation of the time-dependent convective-diffusion equation for surfactant transport along a deforming interface”. In: *Physics of Fluids A* 2.1 (1990), pp. 111–112.
- [3] Wikipedia contributors. *Laplace's spherical harmonics — Wikipedia, The Free Encyclopedia*. [https://en.wikipedia.org/wiki/Spherical\\_harmonics](https://en.wikipedia.org/wiki/Spherical_harmonics).

# Appendix

## A) Use of AI

The overall report was prepared with a limited assistance from AI systems. Its support was used in two ways:

- To check the derivation and the integration steps of the interfacial transport equation for  $\Gamma(\theta)$  and to verify the resulting surface-concentration formula.
- To improve clarity and flow in selected sections (e.g., Abstract and Introduction) without altering the technical content.

All modeling choices, assumptions, parameter selections and final conclusions are the author's own. No figures or references were generated by AI and all sources cited in the report were located and verified independently.

## B) Pole regularity condition

The pole regularity condition is

$$\frac{d\Gamma}{d\theta}(\theta) = \frac{d\Gamma}{d\theta}(\pi) = 0$$

which says the slope is zero at the poles (horizontal tangent). On a sphere, the axisymmetric surface Laplacian is [3]:

$$\nabla_s^2 \cdot \Gamma = \frac{1}{\sin \theta} \frac{d}{d\theta} \left( \sin \theta \frac{d\Gamma}{d\theta} \right)$$

For  $\nabla_s^2 \Gamma$  to stay finite as  $\theta \rightarrow 0, \pi$  it is necessary that  $\sin(\theta) \frac{d\Gamma}{d\theta} \rightarrow 0$  at the poles. Given the first order ODE used in (5) and  $u_\theta = a \cdot \sin(\theta)$ , the right hand side of the equation is  $\propto \sin \theta$ . Therefore:

$$\frac{d\Gamma}{d\theta} = \Gamma k \sin(\theta) \quad (k = a P e_s)$$

which automatically gives  $\frac{d\Gamma}{d\theta}(\theta, \pi) = 0$

## C) Derivation

With the assumption of a spherical interface of radius  $R$ , bearing an insoluble surfactant with surface concentration  $\Gamma(\theta)$ , where  $\theta$  is the polar angle. The system is axisymmetric and the total surfactant present on the interface is conserved.

Defining  $\bar{\Gamma}$  to be the surface-averaged concentration. The unknown constant  $C$  in (6) for  $\Gamma(\theta)$  is determined by enforcing this conservation law [2].

## Surface element and Area

In spherical coordinates the surface area element is

$$dA = R^2 \sin \theta \, d\theta \, d\phi.$$

The total surface area of the sphere is

$$A = \int_0^{2\pi} \int_0^\pi R^2 \sin \theta \, d\theta \, d\phi = 4\pi R^2.$$

## Total surfactant and Conservation

Under axisymmetry, the total amount of surfactant on the surface is

$$\begin{aligned} \iint_S \Gamma(\theta) \, dA &= \int_{\phi=0}^{2\pi} \int_{\theta=0}^\pi \Gamma(\theta) R^2 \sin \theta \, d\theta \, d\phi \\ &= 2\pi R^2 \int_0^\pi \Gamma(\theta) \sin \theta \, d\theta. \end{aligned}$$

Because the surfactant is insoluble (no exchange with the bulk), this must equal the surface area times the average surface concentration  $\bar{\Gamma}$ :

$$\iint_S \Gamma(\theta) \, dA = A \bar{\Gamma} = 4\pi R^2 \bar{\Gamma}.$$

## Integral constraint & Determination of $C$

Equating the two expressions gives

$$2\pi R^2 \int_0^\pi \Gamma(\theta) \sin \theta \, d\theta = 4\pi R^2 \bar{\Gamma}.$$

Divide both sides by  $2\pi R^2$  to obtain the integral constraint:

$$\boxed{\int_0^\pi \Gamma(\theta) \sin \theta \, d\theta = 2 \bar{\Gamma}.}$$

Hence,  $C$  is chosen so that the form of  $\Gamma(\theta)$  used satisfies this equation.

## D) Hand calculations

### Calculation of $\bar{\Gamma}$

The maximum packing concentration is obtained from:

$$\Gamma_{\max} = \frac{1}{N_A a_m} \quad (8)$$

where  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$  (Avogadro's number),

Assuming a small ionic type like SDS/CTAB, which are common contaminants in water systems, Then the molecular cross sectional area  $a_m = 0.5 \text{ nm}^2 = 0.5 \times 10^{-18} \text{ m}^2$  (area per molecule)[1].

$$\begin{aligned}\Gamma_{\max} &= \frac{1}{(6.022 \times 10^{23})(0.5 \times 10^{-18})} \\ &= \frac{1}{3.011 \times 10^5} \\ &= 3.32 \times 10^{-6} \text{ mol/m}^2\end{aligned}$$

Taking 60% of  $\Gamma_{\max}$ :

$$\begin{aligned}\bar{\Gamma} &= 0.6 \times 3.32 \times 10^{-6} \\ &= 2.0 \times 10^{-6} \text{ mol/m}^2\end{aligned}$$

1. Pre-factor( $k$ )(7):

$$\begin{aligned}k &= 3.6 \\ \sinh(k) &= \sinh(3.6) = 18.285 \\ \frac{k}{\sinh(k)} &= \frac{3.6}{18.285} = 0.1968\end{aligned}$$

2. At  $\theta = 0^\circ$  ( $\cos 0^\circ = 1$ )

$$\begin{aligned}\Gamma(0^\circ) &= (2.0 \times 10^{-6})(0.1968)e^{-3.6} \\ &= 2.0 \times 10^{-6} \times 0.1968 \times 0.0273 \\ &= 0.0107 \mu\text{mol/m}^2\end{aligned}$$

3. At  $\theta = 45^\circ$  ( $\cos 45^\circ = 0.7071$ )

$$\begin{aligned}\Gamma(45^\circ) &= (2.0 \times 10^{-6})(0.1968)e^{-2.5455} \\ &= 2.0 \times 10^{-6} \times 0.1968 \times 0.0785 \\ &= 0.0309 \mu\text{mol/m}^2\end{aligned}$$

4. At  $\theta = 90^\circ$  ( $\cos 90^\circ = 0$ )

$$\begin{aligned}\Gamma(90^\circ) &= (2.0 \times 10^{-6})(0.1968)(1) \\ &= 0.3936 \mu\text{mol/m}^2\end{aligned}$$

5. At  $\theta = 135^\circ$  ( $\cos 135^\circ = -0.7071$ )

$$\begin{aligned}\Gamma(135^\circ) &= (2.0 \times 10^{-6})(0.1968)e^{2.5455} \\ &= 2.0 \times 10^{-6} \times 0.1968 \times 12.749 \\ &= 5.010 \mu\text{mol/m}^2\end{aligned}$$

6. At  $\theta = 180^\circ$  ( $\cos 180^\circ = -1$ )

$$\begin{aligned}\Gamma(180^\circ) &= (2.0 \times 10^{-6})(0.1968)e^{3.6} \\ &= 2.0 \times 10^{-6} \times 0.1968 \times 36.598 \\ &= 7.202 \mu\text{mol/m}^2\end{aligned}$$