

Article

Inclination-Driven Thin-Film Dynamics: Geometry-Induced Regime Ordering in the (Bo, Pe, Da) Space

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Abstract

We develop a leading-order continuum framework for thin-film hydrodynamics on inclined solid substrates, integrating capillarity, intermolecular forces, gravitational symmetry breaking, confined transport, and stochastic wetting into a single formulation. Starting from lubrication theory with capillary curvature and disjoining-pressure interactions, we obtain a lubrication-scale thin-film equation that incorporates inclination-driven advection, nanoscale stabilization, and humidity-controlled source–sink fluxes. A dimensionless analysis shows that, within the long-wave lubrication approximation, inclination induces a coordinated leading-order coupling among the Bond (Bo), Péclet (Pe), and Damköhler (Da) numbers. This coupling defines a characteristic inclination-angle-dependent scaling trajectory $\Gamma(\theta)$ in the (Bo, Pe, Da) space: material parameters set the system's position along this curve, while the geometric constraint organizes the ordering of hydrodynamic, transport, and confinement regimes. We further derive leading-order crossover criteria associated with transport transitions ($Pe \simeq 1$) and reactive-confinement loss ($Da \simeq 1$), providing explicit regime boundaries that can be evaluated for representative parameter ranges. A representative parameterization of an ultrathin atmospheric electrolyte film is then used to make these crossovers explicit, yielding illustrative inclination thresholds that depend on the chosen parameter set. Coupling the deterministic structure to a minimal stochastic closure captures intermittent wet–dry dynamics under environmental forcing. In this closure, inclination selectively accelerates the drying pathway through the drainage time (and thus drying rate λ_{dry}), while rewetting remains primarily humidity-controlled, to leading order, providing a scaling-based description of wet-state persistence and time-of-wetness versus θ . The resulting framework provides a continuum-scale physical description of confined films under geometric asymmetry, relevant to wetting, interfacial drainage, confined transport, and thin-film systems in which symmetry breaking and coupled interfacial–transport processes coexist.

Keywords: thin liquid films; inclined substrates; lubrication theory; thin-film stability; confined transport; wet–dry intermittency; Bond number; Péclet number; Damköhler number



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1. Introduction

Thin liquid films on solid surfaces constitute a canonical setting for studying the interplay between geometry, intermolecular forces and hydrodynamics. The behavior of the films governs wetting, adhesion, drainage, lubrication, interfacial transport and rupture, and has long served as a testbed for theories of capillarity, surface forces and thin-film flow [1–3]. The main contribution of this paper is the identification of an inclination-driven trajectory $\Gamma(\theta)$, which induces a coupled evolution of the Bond (Bo), Péclet (Pe) and Damköhler (Da) numbers, in contrast to conventional treatments where these groups are considered independent control parameters. When the film thickness reaches micro- and nanometric scales, the balance between capillary curvature, van der Waals interactions and viscous dissipation becomes highly sensitive to perturbations. Even considerably weak geometric asymmetries can reorganize drainage pathways, stability criteria and rupture dynamics [4–6].

Among such asymmetries, inclination plays a distinctive physical role. Rather than acting as a minor geometric detail, inclination introduces a symmetry-breaking field that couples directly to the drainage flux through the tangential gravitational forcing $\rho g \sin \theta$, where ρ is the liquid density, g is the acceleration due to gravity, and θ is the substrate inclination angle. Classical investigations typically treat thin films in horizontal or weakly perturbed geometries [3,7,8], but natural and technological interfaces—ranging from atmospheric electrolyte layers to evaporating or deliquescent coatings—rarely remain horizontal. Such films undergo cycles of thinning, rupture, rewetting and coalescence under the combined action of gravity, capillarity and disjoining pressure [7–10].

Experimental observations and modeling studies indicate that inclination strongly affects wet-film behavior: inclined surfaces tend to display faster thinning, earlier rupture, and shorter wet-state persistence than horizontal substrates [11,12]. Related thin-film regimes also arise in lubrication systems [10], colloidal films and related viscous liquid-film systems [13], confined interfacial transport [14], evaporating and deliquescent layers, and thin-film flows governed by competing advection–diffusion mechanisms [15,16]. Recent studies have also demonstrated geometry-controlled liquid transport on structured surfaces, including multi-directional spreading enabled by engineered microstructures [17].

Despite this diversity, many treatments study capillarity, disjoining pressure, gravitational drainage, confined electrostatics and stochastic wetting separately, without explicitly clarifying how geometric asymmetry reorganizes these mechanisms in a coordinated way.

The present study identifies a leading-order structural property of lubrication-type thin-film models under inclination. The framework is formulated within the continuum lubrication regime and is therefore restricted to viscous thin liquid films for which long-wave hydrodynamic assumptions apply. In particular, we show that the dimensionless groups governing transport, stability and confinement do not vary independently when the substrate is inclined.

A central feature of the present framework is that inclination simultaneously reweights transport, stability and confinement: it strengthens tangential drainage (via Bo), shifts the advection–diffusion hierarchy (via Pe), and modifies reactive accessibility under confinement (via Da). Although these dimensionless groups are often treated as independently adjustable control parameters, their dependence on film thickness and drainage implies that they are not fully independent under inclination. Here, we show that, at leading order within lubrication theory, inclination does not explore the full (Bo, Pe, Da) parameter space but instead induces a geometry-dependent scaling trajectory $\Gamma(\theta)$. This reduction provides a practical organizing structure for identifying regime ordering and crossover conditions without scanning the entire parameter space.

We develop a continuum-scale, leading-order framework that consolidates these mechanisms within a single continuum formulation. Starting from lubrication theory with capillary curvature and disjoining-pressure interactions, we derive the governing thin-film equation in a form that makes inclination-driven advection, nanoscale stabilization and humidity-controlled source–sink fluxes explicit. A main outcome of the study is that inclination induces a coordinated, leading-order coupling of the Bo, Pe and Da numbers inherited directly from the structure of the lubrication flux. As a consequence, the system evolves along an inclination-dependent scaling path $\Gamma(\theta)$ in the (Bo, Pe, Da) space, providing a systematic basis for investigating stability, drainage, confined transport and reactive accessibility under geometric asymmetry.

The main findings are as follows.

- (i) Inclination enforces a coordinated reweighting of the control groups such that (Bo, Pe, Da) evolve along a single geometry-imposed scaling path $\Gamma(\theta)$ rather than varying independently.
- (ii) This reweighting produces an ordered sequence of transport and confinement crossovers ($Pe \simeq 1$, $Da \simeq 1$) that can be evaluated directly from material and environmental parameters.
- (iii) The same structure provides closure to a minimal stochastic wet–dry model by linking the drying rate λ_{dry} to the films by electrical double-layer overlap, thereby yielding leading-order scaling trends for wet-state persistence and time-of-wetness as functions of θ .

Beyond conceptual unification, the formulation yields quantitative regime criteria. In particular, the inclination-driven scaling of Pe and Da provides explicit crossover conditions separating diffusion-dominated, mixed and advection-dominated transport, as well as the progressive loss of reactive confinement as Da decreases. We then couple the deterministic thinning dynamics to a minimal stochastic wet–dry model, in which inclination selectively accelerates the drying pathway via the drainage time while leaving rewetting largely humidity-controlled. This deterministic–stochastic coupling is intended as a leading-order description and does not account for all possible environmental or material-specific effects.

The resulting formulation is general at the level of continuum thin-film hydrodynamics and provides a leading-order physical framework for understanding geometric asymmetry in confined films across hydrodynamics, interfacial physics and viscous thin liquid films in the continuum lubrication regime. While the present study emphasizes analytical structure and scaling, the governing equations also provide a direct basis for targeted asymptotic or numerical analyses in specific material contexts. The present framework is not intended for molecularly thin layers, such as self-assembled monolayers or supported lipid bilayers, nor for solid or glassy films, where continuum hydrodynamics no longer applies. In corrosion-related contexts, the model describes the electrolyte film dynamics rather than inhibitor-layer behavior or detailed electrochemical kinetics.

2. Governing Equations and Coupled Film Dynamics

Thin-film dynamics on an inclined solid substrate arise from the coupled action of viscous flow, capillary curvature, intermolecular forces, gravitational symmetry breaking and humidity-controlled source–sink fluxes. This section derives the governing equations from lubrication theory and establishes the structure required for the dimensionless analysis in Section 3.

2.1. Lubrication Framework and Gravitational Symmetry Breaking

Consider a liquid film of local thickness $h(x, t)$, with x the space coordinate and t the time, on a substrate inclined at an angle θ . Under the long-wave approximation $h/L \ll 1$, with L the lateral scale, and $|\partial_x h| \ll 1$, with $\partial_x \equiv \partial/\partial x$, the lateral flow is appropriately

described by lubrication theory. A schematic of the inclined thin-film geometry and the relevant forces is shown in Figure 1.

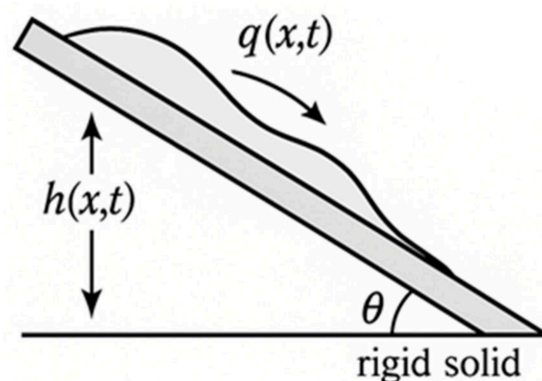


Figure 1. Schematic representation of a thin liquid film on an inclined solid substrate. See text for details.

The depth-averaged volumetric flux per unit width, denoted $q(x, t)$, is [3,4]

$$q(x, t) = -\frac{h^3}{3\mu} \partial_x (\gamma \partial_{xx} h + \Pi(h)) + \frac{\rho g \sin \theta}{3\mu} h^3, \quad (1)$$

where μ is viscosity, γ is surface tension, and $\rho g \sin \theta$ is the tangential gravitational forcing. Mass conservation then gives

$$\partial_t h + \partial_x q = S(x, t), \quad (2)$$

with $S(x, t)$ representing condensation–evaporation fluxes. Inclination enters solely through the $\sin \theta$ term, acting as a symmetry-breaking field that biases drainage without altering capillary or intermolecular contributions. This formulation applies broadly to ultrathin films dominated by viscous, capillary and van der Waals forces [1,2,5].

This structure also makes transparent that inclination enters the governing flux only through gravitational contribution, which becomes the leading-order source of θ -dependence in the dimensionless groups derived in Section 3.

The thin-film flux in Equation (1) is derived under the standard lubrication assumptions of Newtonian viscosity, no-slip at the solid surface, small interfacial slopes $|\partial_x h| \ll 1$, negligible inertia ($\text{Re} \ll 1$), and a separation of scales $h/L \ll 1$. Slip, if present, modifies only the mobility prefactor $h^3/3\mu$ and does not alter the leading-order structure of the capillary, disjoining-pressure or gravitational terms. The formulation is not intended to describe molecularly thin precursor layers or regimes in which continuum hydrodynamics, the disjoining-pressure model, or the classical mobility law break down. Within these constraints, Equation (1) captures the dominant balance of forces governing micrometric and nanometric films on inclined substrates and provides the appropriate starting point for the nondimensional analysis of Section 3.

From Equation (1), a characteristic downslope velocity scale follows immediately from the gravitational mobility,

$$U_\theta \sim \frac{\rho g H^2}{3\mu} \sin \theta, \quad (3)$$

where H is the representative film thickness, and the corresponding drainage timescale is $T_\theta \sim L/U_\theta$. These two quantities provide direct quantitative access to inclination-controlled regime boundaries used below: $\text{Pe}(\theta) \sim U_\theta L/D$, with D the molecular diffusivity, U_θ the drainage velocity associated with gravitational forcing, and $\text{Da}(\theta) \sim kH/U_\theta$, with k the

reaction rate. Thus, even before full numerical integration, the governing structure yields measurable inclination-dependent crossover criteria.

2.2. Capillary Curvature and Intermolecular Forces

Capillary pressure is

$$P_c = -\gamma \partial_{xx} h, \quad (4)$$

which stabilizes short-wavelength disturbances. Intermolecular forces enter through the disjoining pressure [2],

$$\Pi(h) = -\frac{A}{6\pi h^3} + \Pi_{\text{rep}}(h), \quad (5)$$

with A the Hamaker constant and $\Pi_{\text{rep}}(h)$ denoting electrostatic or structural repulsion [6,18].

Related disjoining-pressure models for both volatile and nonvolatile thin films, including dry-spot growth and film-disappearance scenarios, are discussed in [19].

In the absence of gravity, the competition between the capillary pressure P_c and the disjoining pressure $\Pi(h)$, defined in Equations (4) and (5), respectively, yields the classical spinodal-dewetting instability [7,9].

Inclination does not modify $\Pi(h)$ or capillarity itself; instead, it accelerates access to the ultrathin regime where $\Pi'(h)$ controls stability, thereby shortening rupture times and biasing instability pathways downslope through the gravitational flux [3,4].

2.3. Source–Sink Terms and Environmental Coupling

Humidity-driven processes enter through

$$S = S_{\text{cond}}(RH, T) - S_{\text{evap}}(T, h), \quad (6)$$

describing condensation/deliquescence and evaporation [20,21].

These fluxes control rewetting cycles, rupture recovery and wet/dry intermittency—behaviors characteristic of humidity-driven electrolyte films on exposed surfaces [11,12].

2.4. Confined Electrostatics in Ultrathin Films

For electrolyte films, the electric potential $\phi(x, t)$ satisfies

$$\nabla \cdot [\kappa(h) \nabla \phi] = 0, \quad (7)$$

where $\kappa(h)$ is the thickness-dependent conductivity, reduced in nanometric films by electrical double-layer overlap [2], with the boundary conditions

- for solid–liquid interface: $-\kappa \partial_n \phi = j_{\text{int}}$ and
- for liquid–air interface: $\partial_n \phi = 0$.

Electric relaxation is much faster than hydrodynamic dynamics [14], justifying the quasi-static approximation.

2.5. Ionic Advection–Diffusion and Reactive Transport

The solute concentration c satisfies

$$\partial_t c + \partial_x(uc) = D \partial_{xx} c + R(c, h, \phi), \quad (8)$$

where $u = q/h$ is the depth-averaged lateral velocity and R represents reactive or electrochemical processes.

Inclination modifies solute retention through the ratio uL/D , linking gravitational drainage to mass-transport resistance and reactive confinement [15,16].

2.6. Structure of the Coupled Thin-Film Fields

The coupled fields

$$\{h(x, t), c(x, t), \phi(x, t)\} \quad (9)$$

provide a complete continuum-scale description of the dynamics of inclined thin films. Within the lubrication framework, Equation (9) captures the leading-order balance among viscous flow, capillarity, intermolecular forces, gravitational forcing and confined transport.

This formulation is valid under the usual long-wave assumptions: small interfacial slopes, negligible inertia, Newtonian viscosity and film thicknesses sufficiently large for continuum hydrodynamics to apply. Molecularly thin precursor layers, strong-slip conditions and Knudsen-scale effects lie outside the range of applicability of this leading-order model.

The nondimensional structure emerging from these equations is developed in Section 3.

3. Dimensionless Formulation and the Inclination-Driven Trajectory

The dimensionless structure of the governing equations reveals how inclination reshapes the relative contributions of capillarity, intermolecular forces, gravitational drainage and confined transport. When expressed using appropriate characteristic scales, the thin-film equations reduce to a compact form governed by three natural dimensionless groups: the Bo, Pe and Da numbers.

The coordinated dependence of these groups on the inclination angle defines a leading-order inclination-dependent scaling trajectory in the (Bo, Pe, Da) parameter space. This scaling structure provides a practical organizing description of inclined thin-film behavior, setting the structure developed in the subsections below.

3.1. Characteristic Scales and Nondimensional Variables

A natural starting point for the nondimensional analysis is to identify the characteristic scales that describe the geometry and dynamics of the inclined film. Let $T = L/U_\theta$ denote the corresponding advective timescale. Because the gravitational contribution to the lubrication flux scales as $\rho g h^3 \sin \theta$, the velocity scale is written as $U_\theta = U_0 \sin \theta$, where U_0 is an inclination-independent reference velocity. This choice preserves the leading-order dependence on θ , ensuring that inclination appears explicitly—and solely—through gravity-driven advection in the dimensionless formulation.

Using these scales, the dimensional variables are expressed in nondimensional form as

$$x = Lx', h = Hh', t = Tt', q = UH q', \quad (10)$$

where primes are omitted after substitution.

With these definitions, the mass-conservation law becomes

$$\partial_t h + \partial_x q = \text{Da}_0 S^*(RH, T, h), \quad (11)$$

where Da_0 is a nondimensional source–sink strength and $S^*(RH, T, h)$ is an $\mathcal{O}(1)$ dimensionless source–sink function representing the humidity-controlled balance of condensation/deliquescence and evaporation (see Section 2.3).

The corresponding nondimensional flux takes the form

$$q = -h^3 \left[\text{Ca}^{-1} \partial_{xxx} h - \partial_x \Pi^*(h) - \text{Bo}_0 \sin \theta \right], \quad (12)$$

with

$$\text{Ca} = \frac{\mu U}{\gamma}, \text{Bo}_0 = \frac{\rho g H^2}{\gamma}, \Pi^*(h) = \frac{H}{\gamma} \Pi(h). \quad (13)$$

Here Bo_0 is a reference Bond number based on the film thickness scale, while inclination enters explicitly through the multiplicative factor $\sin \theta$.

In this representation, inclination enters only through the effective gravitational contribution $Bo_0 \sin \theta$, isolating the geometric contribution to the force balance independently of the specific material parameters.

This formulation makes explicit that the inclination dependence of all transport-related quantities is inherited through the scaling $U_\theta = U_0 \sin \theta$. As a consequence, the associated dimensionless groups (Pe, Da) acquire a coordinated dependence on θ , while the governing equations retain a fixed structure. Variations in θ therefore move the system along a single constrained path in parameter space, rather than sampling independent combinations of transport, reaction and hydrodynamic effects.

3.2. Balance Between Capillarity, Intermolecular Forces and Gravity

The nondimensional flux highlights the competing roles of capillary curvature, intermolecular forces and gravitational drainage in determining thin-film dynamics.

In nondimensional form, these contributions scale as

- $Ca^{-1} \partial_{xxx} h$ (capillarity);
- $-\partial_x \Pi^*(h)$ (intermolecular forces);
- $-Bo_0 \sin \theta$ (gravity).

Meanwhile, viscous resistance enters through the geometric factor h^3 .

Because these terms enter additively into the flux, inclination modifies the relative magnitude of the competing contributions rather than their absolute scale. As θ increases, the effective gravitational contribution grows through $Bo_0 \sin \theta$, while the capillary and intermolecular terms remain unchanged. This introduces a progressive reweighting of the force balance:

- the gravitational contribution strengthens monotonically;
- the effective stabilizing influence of capillarity weakens in relative terms; and
- the film becomes increasingly sensitive to intermolecular attraction at small thickness.

The inclination angle θ therefore acts as a natural organizing parameter for dynamics, altering the hierarchy of competing forces without affecting the structure of the governing equations. The condition $Bo_0 \sim 1$ defines a reference scale at which gravitational and capillary effects become comparable, while the effective contribution remains modulated by $\sin \theta$.

3.3. Solute Transport and the Péclet Number

Solute transport in the draining film is governed by the interplay between advection, diffusion and reaction. In nondimensional form, the transport equation reads

$$\partial_t c + \partial_x (uc) = Pe^{-1} \partial_{xx} c + R(c, h, \phi) \quad (14)$$

and the Pe number,

$$Pe = U_\theta L / D, \quad (15)$$

measures the relative strength of advective drainage to diffusive redistribution.

Because the characteristic velocity arises from the gravitational component of the lubrication flux (Section 2.1), its inclination dependence is inherited directly from the factor $\sin \theta$. Consequently,

$$Pe(\theta) = Pe_0 \sin \theta, \quad (16)$$

where $Pe_0 = U_0 L / D$ is the reference Péclet number associated with the inclination-independent velocity scale U_0 . Thus, inclination drives the system across three distinct transport regimes:

- Diffusion-dominated regime ($Pe \ll 1$). Concentration gradients relax efficiently, and transport is primarily controlled by confinement through $h(x, t)$.
- Intermediate regime ($Pe \sim 1$). Advection and diffusion compete, generating longitudinal concentration gradients and coupling transport to film morphology.
- Advection-dominated regime ($Pe \gg 1$). Solutes are rapidly displaced downslope, residence times shorten, and the system becomes sensitive to even small variations in inclination.

These regimes arise directly from the nondimensional structure of the governing equations and reflect the geometric amplification of transport associated with increasing θ . The condition $Pe(\theta) \approx 1$ marks the transition from solute retention to advective flushing, providing a direct criterion for when inclined films cease to accumulate dissolved species.

3.4. Reactive Confinement and the Damköhler Number

Reactive processes within the film introduce an additional nondimensional parameter, the Da number, which compares the timescale of reaction to the timescale of advective transport. For a reaction rate k , the nondimensional form is

$$Da = kL / U_\theta. \quad (17)$$

Because the drainage velocity U_θ is set by gravitational forcing and increases monotonically with the inclination angle θ , the Damköhler number decreases accordingly:

$$Da(\theta) \propto \frac{Da_0}{\sin \theta}, \quad (18)$$

where $Da_0 = kL / U_0$. This has direct implications for reactive confinement:

- Reaction-dominated regime ($Da \gg 1$). Solute residence times exceed reactive timescales; reactivity is governed primarily by film thickness and intermolecular interactions
- Transport-limited regime ($Da \ll 1$). Advection removes solute faster than it can react; reaction becomes constrained by supply rather than kinetics.
- Coupled regime ($Da \sim 1$). Comparable timescales lead to strong sensitivity to local variations in $h(x, t)$, $u(x, t)$ and confined electrostatics.

The inclination-controlled shift from reaction-dominated to transport-dominated behavior is therefore an intrinsic feature of inclined thin-film systems, arising directly from the nondimensional structure of the governing equations. The shift also underpins the shortening of reactive intervals and the reduction in wet-state persistence studied in Section 4 below.

The inclination-driven decrease in $Da(\theta)$ implies that increasing θ shifts the system from reaction-dominated to transport-limited behavior, even when intrinsic kinetics remain unchanged.

3.5. Inclination-Driven Trends in (Bo, Pe, Da) Space

The nondimensional structure derived in Sections 3.1–3.4 reveals a coordinated dependence of the Bo , Pe and Da numbers on the inclination angle. Here Bo_0 , Pe_0 , and Da_0 denote inclination-independent reference values set by material, transport, and kinetic parameters. To leading order, the corresponding inclination-dependent effective quantities are

$$Bo_{\text{eff}}(\theta) = Bo_0 \sin \theta, Pe(\theta) = Pe_0 \sin \theta, Da(\theta) = \frac{Da_0}{\sin \theta}.$$

The gravitational forcing enters the lubrication flux through the effective contribution $Bo_{\text{eff}}(\theta)$. Thus, variations in θ induce a coupled change in the relative importance of transport, reaction, and gravitational forcing.

These relations follow directly from the nondimensional lubrication flux (Section 3.1), in which gravitational forcing contributes solely through the term $Bo_0 \sin \theta$, while the velocity scale $U_\theta = U_0 \sin \theta$ induces the corresponding inclination dependence of Pe and Da .

Under the assumptions of the long-wave lubrication approximation (Newtonian viscosity, no slip at the substrate, $h/L \ll 1$, negligible inertia, and source–sink terms that do not introduce additional intrinsic length or velocity scales), this coordinated dependence defines a leading-order inclination-dependent scaling trajectory $\Gamma(\theta)$ in the (Bo, Pe, Da) space. Figure 2 summarizes this structure: Figure 2a shows the projection of $\Gamma(\theta)$ onto the Bo – Pe plane, Figure 2b shows the associated $Da(\theta)$ scaling along $\Gamma(\theta)$, and Figure 2c provides a schematic summary of the coordinated reweighting of the three dimensionless groups with inclination.

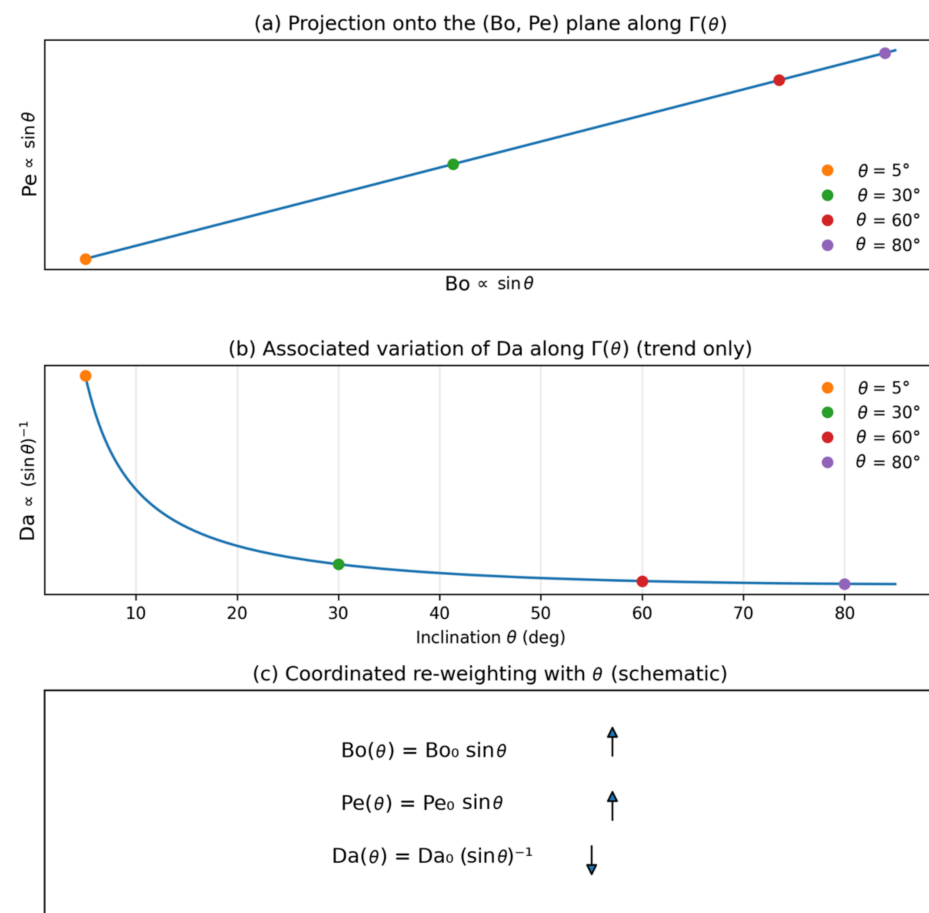


Figure 2. Inclination-dependent scaling trajectory in the $(Bo|Pe|Da)$ space. (a) Projection onto the (Bo, Pe) plane along $\Gamma(\theta)$, showing the coordinated increase in the effective gravitational contribution and advective transport with inclination. (b) Associated variation in $Da(\theta)$ along the same trajectory, illustrating the corresponding decrease in the relative importance of reaction. (c) Schematic summary of the coordinated leading-order reweighting with θ , highlighting that inclination explores a restricted subset of parameter space defined by the scaling relations of the lubrication framework. Here, Bo_0 , Pe_0 , and Da_0 denote inclination-independent reference values set by material, transport, and kinetic parameters; panel (c) therefore summarizes the leading-order inclination dependences $Bo(\theta) = Bo_0 \sin \theta$, $Pe(\theta) = Pe_0 \sin \theta$, and $Da(\theta) = Da_0 / \sin \theta$, which altogether define the trajectory $\Gamma(\theta)$. See text for details.

The structure of this trajectory arises generically at leading order within the lubrication framework, as a consequence of the form of the gravitational contribution to the flux. However, the quantitative position of any specific system along it depends on material parameters such as viscosity, intermolecular interactions, diffusivity, and reaction rates.

Thus, rather than claiming that all thin-film systems evolve identically, we emphasize that inclination induces a coordinated leading-order reweighting of the governing contributions, while material properties determine the quantitative location along the resulting trajectory. This leading-order coupling arises directly from the structure of the lubrication flux: gravitational forcing increases with inclination ($Bo \uparrow$), advection strengthens accordingly ($Pe \uparrow$), and the relative importance of reaction decreases ($Da \downarrow$), where $\uparrow$ and $\downarrow$ denote increasing and decreasing trends with θ , respectively. Altogether, these coordinated shifts reorganize the balance between drainage, transport and confined reactivity.

The resulting inclination-dependent scaling trajectory provides a compact and physically transparent representation of the underlying dynamics. The inclination captures the progressive transition from capillarity-dominated flow at relatively low inclination to advection-dominated drainage at higher inclination and provides a consistent framework for interpreting the associated loss of reactive confinement and shortening of residence times discussed in Section 5. A key implication is that inclination does not sample arbitrary combinations of (Bo , Pe , Da), but instead explores a restricted subset defined by the scaling relations above. This reduction should be interpreted as a leading-order consequence of the lubrication framework, rather than as a strict one-dimensional manifold applicable to all thin-film systems. While the inclination dependence follows directly from the underlying scaling, its consequence is non-trivial: it constrains the system to a one-parameter trajectory $\Gamma(\theta)$, thereby imposing a deterministic ordering of transport and reactive regimes that would not arise if the dimensionless groups were varied independently. This structure should therefore be interpreted as a leading-order scaling result, valid within the continuum lubrication framework and for regimes in which the dominant balances are captured by the thin-film approximation. Outside this regime—for example, in strongly inertial flows, non-continuum systems, or configurations with additional inclination-dependent physics—the trajectory $\Gamma(\theta)$ may no longer apply.

3.6. Representative Parameterization and Crossover Angles

To provide a representative quantitative anchor for the leading-order framework, we consider an ultrathin atmospheric electrolyte film at 25 °C. The chosen parameter values are representative and serve to illustrate the scaling structure and crossover ordering, rather than to provide system-specific or experimentally calibrated predictions. The fluid properties are taken as representative aqueous values, namely $\rho = 997 \text{ kg m}^{-3}$, $\mu = 0.89 \times 10^{-3} \text{ Pa s}$, and $\gamma = 71.97 \times 10^{-3} \text{ N m}^{-1}$, consistent with standard thermophysical data for water [22], while the molecular diffusivity is taken as $D = 2.03 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, a representative value commonly adopted for chloride transport in aqueous media [23]. These values are selected to be consistent with typical orders of magnitude reported in thin-film and interfacial transport studies, but no specific material system is assumed.

The characteristic thickness $H = 1 \text{ }\mu\text{m}$ is adopted as a representative thin-film scale relevant to atmospheric corrosion [11,12], while $L = 1 \text{ mm}$ is introduced here as a representative surface-transport length for the illustrative calculation. The complete parameter set is summarized in Table 1.

Table 1. Representative parameters used to illustrate the inclination-driven crossover structure.

Parameter	Value
Representative film thickness H	1 μm
Lateral length scale L	1 mm
Liquid density ρ	997 kg m^{-3}
Viscosity μ	$0.89 \times 10^{-3} \text{ Pa s}$
Surface tension γ	$71.97 \times 10^{-3} \text{ N m}^{-1}$
Diffusivity D	$2.03 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
Reaction rate k^a	10^{-3} s^{-1}

^a adopted here only to illustrate the reactive branch.

For this representative parameter set, the reference drainage velocity scale is

$$U_0 = \frac{\rho g H^2}{3\mu} \approx 3.66 \times 10^{-6} \text{ m s}^{-1},$$

which gives

$$\text{Pe}_0 = \frac{U_0 L}{D} \approx 1.80 \text{ and } \text{Bo}_0 = \frac{\rho g H^2}{\gamma} \approx 1.36 \times 10^{-7}.$$

Accordingly, the inclination-dependent drainage velocity becomes

$$U_\theta = U_0 \sin \theta,$$

so that

$$\text{Pe}(\theta) \approx 1.80 \sin \theta.$$

The transport crossover defined by $\text{Pe} = 1$ therefore occurs at

$$\theta_{\text{Pe}} \approx 33.7^\circ.$$

To illustrate the reactive branch of the trajectory, we further adopt here a representative first-order reaction rate $k = 10^{-3} \text{ s}^{-1}$, used only for the illustrative crossover estimate. This yields

$$\text{Da}(\theta) \approx \frac{0.273}{\sin \theta}.$$

The corresponding reactive crossover $\text{Da} = 1$ then occurs at

$$\theta_{\text{Da}} \approx 15.8^\circ.$$

The resulting inclination-dependent evolution of $\text{Pe}(\theta)$ and $\text{Da}(\theta)$ is shown in Figure 3. The intersections with the unity threshold make the crossover angles θ_{Da} and θ_{Pe} explicit and show that, for this representative case, the reactive crossover precedes the transport crossover. In other words, the system first exits the reaction-dominated regime and only at larger inclinations enters the mixed advection–diffusion regime. At the same time, the Bo number remains considerably small throughout, since $\text{Bo}_0 \approx 1.36 \times 10^{-7}$, indicating that the film remains strongly capillary-dominated even though transport and reactive accessibility are substantially reorganized by inclination.

The example considered is not intended as a system-specific calibration or validation but rather serves as an illustrative example of the crossover ordering implied by the scaling relations. The present study establishes the leading-order scaling structure and the associated regime ordering. Full numerical resolution of Equation (2), with the flux given by Equation (1), yields system-specific quantitative predictions, but is not required for the analytical identification of the inclination-driven trajectory $\Gamma(\theta)$ and its associated

crossover structure. The predicted trends are qualitatively consistent with experimental observations reporting faster drainage, earlier rupture, and reduced wet-state persistence in inclined films [11,12].

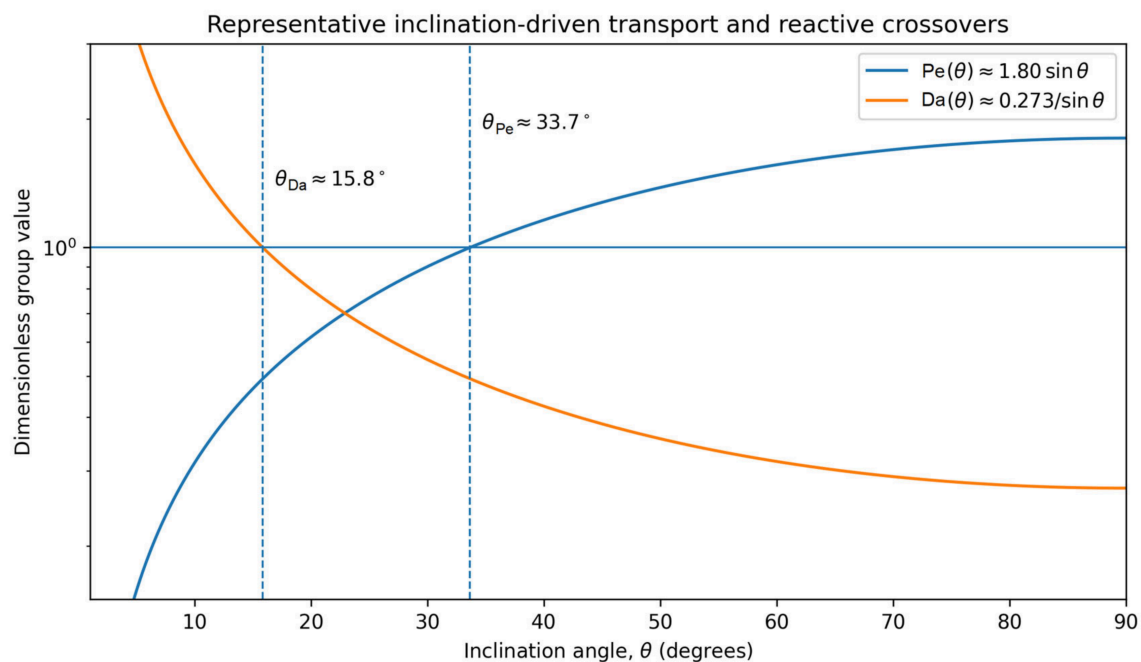


Figure 3. Representative inclination-driven transport and reactive crossovers for the parameter set listed in Table 1. The curves show $Pe(\theta) \approx 1.80 \sin \theta$ and $Da(\theta) \approx 0.273/\sin \theta$. The horizontal line at unity identifies the crossover angles $\theta_{Da} \approx 15.8^\circ$ and $\theta_{Pe} \approx 33.7^\circ$, corresponding to the onset of transport-limited behavior and mixed advection–diffusion transport, respectively.

The numerical crossover angles depend on the chosen values of H , L , D , and k , and should therefore be interpreted as representative rather than universal angles.

3.7. Implications for Film Stability, Transport and Rupture

The inclination-driven variations in Bo , Pe and Da summarized by the leading-order trajectory $\Gamma(\theta)$ have direct consequences for film stability, drainage dynamics and confined transport. As θ increases, gravitational forcing strengthens through Bo , advection becomes progressively dominant through Pe , and the relative importance of reaction diminishes through Da . These coordinated shifts reorganize the hierarchy of physical processes that govern thin-film behavior.

For stability, an increase in Bo accelerates thinning and promotes earlier access to regimes in which intermolecular attractions dominate. This leads to reduced rupture times and asymmetric dewetting fronts, consistent with the gravitational bias introduced in Section 2 and with theoretical predictions for gravity-driven front propagation and instability asymmetry [4,8].

For transport, the increase in Pe shortens residence times and enhances the longitudinal advection of solute, weakening the ability of diffusion to maintain uniform concentration profiles. Confined electrostatics and near-surface interactions become less effective as the film is rapidly displaced downslope.

For reactions, the decrease in Da shifts the system from reaction-dominated behavior at low inclination toward a transport-limited regime at higher inclination. This transition reduces the duration over which solutes can interact within confined, high-resistivity regions and therefore suppresses sustained reactive pathways.

Altogether, these trends suggest an inclination-controlled classification of thin-film regimes, expressed through measurable crossover conditions in (Bo, Pe, Da) , space. This deterministic structure provides the foundation for the stochastic wetting study developed in Section 4 below, where inclination-driven variations in drainage rate and residence time control the statistics of wet–dry cycling and the long-time persistence of reactive intervals.

4. Stochastic Wetting and Time-of-Wetness Dynamics

Thin films exposed to atmospheric forcing rarely evolve as continuous layers. Instead, they undergo intermittent cycles of formation, drainage, rupture and rewetting driven by humidity fluctuations, aerosol deposition and environmental noise. While the deterministic equations in Section 2 describe the deterministic dynamics of the film thickness, those equations cannot capture the discrete transitions between wet and dry states that dominate long-time surface behavior. A stochastic description is therefore required to represent the intermittent nature of atmospheric wetting, particularly on inclined substrates where drainage is strongly enhanced.

Inclination modifies these transitions by reorganizing the drainage flux, accelerating access to rupture thresholds and reducing the residence time of liquid films. The combined deterministic–stochastic structure provides a physically grounded framework for understanding the observed decrease in time-of-wetness with increasing inclination.

4.1. Deterministic Thin-Film Dynamics and Rupture Thresholds

The deterministic dynamics of the film thickness are governed by Equation (2), which describes the continuous thinning of the film between wetting events. Rupture occurs when the local thickness reaches the critical value h_{crit} , set by the balance between van der Waals attraction and capillary curvature. This threshold marks the limit of metastability for ultrathin films and determines the termination of a wet interval in the absence of rewetting.

As was shown in Sections 2 and 3, the gravitational contribution to the flux grows with inclination through the gravitational forcing $\rho g \sin \theta$ in the lubrication flux (Section 2), and equivalently through the inclination dependence of the relevant dimensionless groups introduced in Section 3. The increased downslope advection accelerates thinning and causes the deterministic trajectory $h(t)$ to reach h_{crit} more rapidly as θ increases. In particular, in the drainage-dominated limit the characteristic film-loss time scales as $t_{\text{drain}}(\theta) \sim L/U_\theta$, with $U_\theta \propto \sin \theta$, implying a monotonic decrease in t_{drain} with inclination. Inclination therefore shortens the deterministic component of the wet-state lifetime, independently of environmental factors such as humidity or aerosol deposition.

The inclination dependence of the drainage time plays a central role in the stochastic framework developed in Section 4.2 below: it sets the scale for the drying rate λ_{dry} , which increases monotonically with θ . The deterministic thinning dynamics therefore provide the physical basis upon which the stochastic wet/dry transitions are built.

4.2. Stochastic Transition Between Wet and Dry States

Environmental forcing introduces intrinsic randomness into film re-formation events, primarily through humidity fluctuations, aerosol deposition and vapor-phase transport.

To capture this behavior, the surface is idealized as a two-state stochastic process in which the interface alternates between

- a wet state (W), where a continuous or metastable film exists and
- a dry state (D), where the film has ruptured or is absent.

Transitions between these states occur with rates

$$W \xrightarrow{\lambda_{\text{dry}}} D \text{ and } D \xrightarrow{\lambda_{\text{wet}}} W,$$

where λ_{dry} denotes the effective drying or rupture rate associated with the deterministic drainage process, and λ_{wet} is the rewetting rate associated with condensation or deliquescence [20,21].

Inclination modifies these rates asymmetrically. As was shown in Sections 2 and 3, the gravitational contribution to the flux increases monotonically with $\text{Bo} \sin \theta$, reducing the deterministic drainage time of Section 4.1 and thereby increasing λ_{dry} . In contrast, λ_{wet} depends primarily on humidity, temperature and vapor transport, and is only weakly sensitive to θ [11]. This approximation is expected to hold when film re-formation is governed primarily by external supply mechanisms, such as humidity-driven condensation, deliquescence, or aerosol deposition, rather than by gravity-driven lateral redistribution along the substrate. In systems where rewetting involves significant surface flow, geometrically constrained redistribution, or strong coupling to substrate heterogeneity, the assumption of an approximately inclination-independent λ_{wet} may become less accurate. This asymmetry—an inclination-enhanced drying rate together with an approximately inclination-independent wetting rate—is the stochastic counterpart of the inclination-driven reweighting of the Bo , Pe and Da numbers established in Section 3.

The competition between λ_{dry} and λ_{wet} governs the statistics of intermittent wetting. In particular, the steady-state wet-state probability is

$$P_{\text{wet}} = \frac{\lambda_{\text{wet}}}{\lambda_{\text{wet}} + \lambda_{\text{dry}}}, \quad (19)$$

which decreases systematically with inclination because $\lambda_{\text{dry}}(\theta)$ grows while λ_{wet} remains nearly constant. This two-state Markov process also yields closed-form dwell-time statistics: the mean wet-interval duration is $\langle t_W \rangle = 1/\lambda_{\text{dry}}$, and the mean dry-interval duration is $\langle t_D \rangle = 1/\lambda_{\text{wet}}$. Inclination therefore reduces $\langle t_W \rangle$ deterministically through $\lambda_{\text{dry}}(\theta)$, while leaving $\langle t_D \rangle$ primarily controlled by environmental forcing.

This provides a physically grounded explanation for the pronounced reduction in wet-state persistence observed experimentally in inclined electrolyte films [12], without invoking any chemistry-specific mechanisms.

The structure of this two-state stochastic pathway, together with the deterministic–stochastic closure $\lambda_{\text{dry}}(\theta) \sim t_{\text{drain}}(\theta)^{-1}$, is summarized in Figure 4.

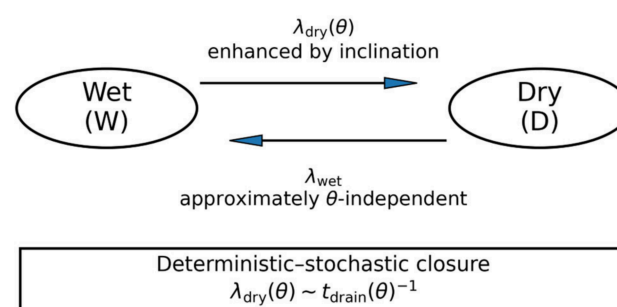


Figure 4. Two-state Markov model for wet–dry intermittency. W denotes the wet (film-present) state and D the dry/ruptured (film-absent) state. The drying/rupture transition $W \rightarrow D$ occurs at rate $\lambda_{\text{dry}}(\theta)$, enhanced by inclination, while rewetting $D \rightarrow W$ occurs at rate λ_{wet} , taken approximately independent of θ . This approximation applies when rewetting is governed mainly by external humidity-driven supply rather than by gravity-driven redistribution along the surface. The deterministic–stochastic closure is $\lambda_{\text{dry}}(\theta) \sim t_{\text{drain}}(\theta)^{-1}$.

The stochastic formulation thus complements the deterministic dynamics by providing a quantitative description of how inclination reshapes the balance between rupture

and re-formation events, establishing the foundation for the time-of-wetness study in Section 4.3 below.

This two-state model is intentionally minimal and assumes Poissonian (memoryless) transitions, with constant wetting and drying rates. In this formulation, the $W \leftrightarrow D$ dynamics constitute a Markov process with exponential waiting times, providing a mean-field description that neglects temporal correlations and long-tailed statistics. Such a closure is appropriate for capturing inclination-controlled shifts in the average wet persistence, but it does not resolve potential non-Markovian effects, such as heavy-tailed waiting times or humidity-driven correlations associated with environmental fluctuations or substrate heterogeneity. These extensions lie beyond the scope of the present paper.

4.3. Wet-State Persistence and Time-of-Wetness

The stochastic description introduced in Section 4.2 determines the persistence of wet states through the competition between the drying and rewetting pathways. In the long-time limit, the wet-state probability is fully controlled by the ratio $\lambda_{\text{wet}}/\lambda_{\text{dry}}$. Since inclination affects only the drying pathway—by shortening the deterministic drainage time introduced in Section 4.1—the wet-state probability inherits a strict geometric dependence, decreasing monotonically with θ .

An illustrative prediction of this monotonic dependence is shown in Figure 5.

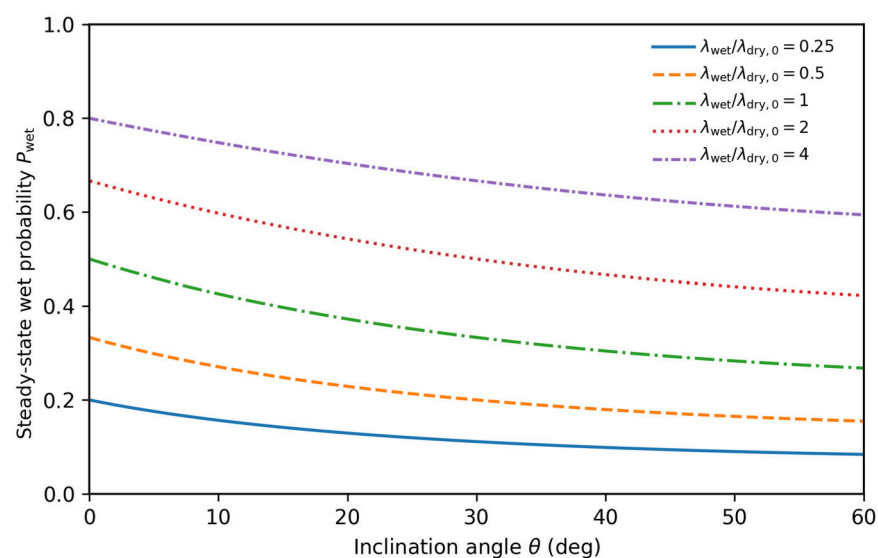


Figure 5. Steady-state wet-state probability $P_{\text{wet}} = \lambda_{\text{wet}} / (\lambda_{\text{wet}} + \lambda_{\text{dry}}(\theta))$ as a function of inclination angle θ for several ratios $\lambda_{\text{wet}}/\lambda_{\text{dry},0}$ as indicated, where $\lambda_{\text{dry},0} \equiv \lambda_{\text{dry}}(\theta = 0)$. Inclination enhances the drying pathway by increasing $\lambda_{\text{dry}}(\theta)$ (through the shorter deterministic drainage time), while λ_{wet} is taken approximately independent of θ , producing a monotonic decline in wet-state persistence. The qualitative trend is robust to the specific functional form of $\lambda_{\text{dry}}(\theta)$, provided λ_{dry} increases monotonically with inclination.

The time-of-wetness (TOW), defined as the fraction of a long interval during which the surface remains wet, coincides with this steady-state wet probability for any stationary two-rate process. Thus, TOW decreases systematically with inclination, reflecting the geometry-driven amplification of the drying pathway rather than any chemistry-specific mechanism. A characteristic crossover inclination θ^* may be defined by the condition $\lambda_{\text{dry}}(\theta^*) \approx \lambda_{\text{wet}}$ marking the transition from predominantly wet to predominantly dry surface occupancy under otherwise unchanged environmental forcing. This behavior is consistent with the pronounced decline in wet-state persistence observed experimentally for electrolyte films on inclined metallic substrates [11,12].

This probabilistic viewpoint completes the connection between deterministic drainage, stochastic rupture and macroscopic wet/dry statistics, providing the basis for the stability and transport consequences examined in Section 5 below.

4.4. Coupling Deterministic Dynamics to Stochastic Transitions

The stochastic transitions characterized by the rates λ_{dry} and λ_{wet} acquire physical meaning only when linked to the deterministic thinning behavior established in Section 4.1. The drainage time $t_{\text{drain}}(\theta)$, defined as the time for a continuous film to reach its rupture threshold, sets the natural scale for transitions out of the wet state. Consequently,

$$\lambda_{\text{dry}} \sim t_{\text{drain}}^{-1}, \quad (20)$$

so that inclination modifies the drying pathway entirely through its influence on the deterministic fluxes derived in Section 2 and the dimensionless reweighting discussed in Section 3. This deterministic closure is central: it fixes the entire inclination dependence of the stochastic model through $t_{\text{drain}}(\theta)$, rather than treating $\lambda_{\text{dry}}(\theta)$ as an empirical fitting function.

In contrast, the rewetting rate is set by vapor-phase processes, condensation kinetics and ambient humidity fluctuations [20,21], none of which couple directly to gravitational asymmetry. The stochastic model therefore inherits a unidirectional sensitivity: inclination accelerates drying but leaves rewetting largely unchanged.

This separation of roles is essential. It provides a mechanistic interpretation for why wet/dry cycling becomes increasingly intermittent with increasing θ , and why time-of-wetness decreases despite unchanged environmental forcing. The deterministic–stochastic link also ensures that statistical quantities such as the wet-state probability, wet-interval distribution, and the long-time TOW (Section 4.3) are governed by geometric rather than material parameters.

4.5. Implications for Interfacial Reactivity and Transport

The intermittent wetting generated by the dynamics described in Sections 4.1–4.4 has direct consequences for transport and reactive processes within ultrathin films. Because solute retention, electrostatic confinement and reaction kinetics all depend on the duration and continuity of the wet state, the progressive decline in wet-state persistence with inclination produces a systematic reorganization of interfacial behavior.

In the relatively low-inclination regime, long wet intervals and relatively infrequent drying events allow ionic confinement and concentration gradients to develop, favoring reaction pathways that require sustained film continuity. As inclination increases, the shortening of wet intervals limits solute residence time and weakens electrostatic confinement, shifting the interfacial response toward transport-controlled, short-residence-time regimes. These effects arise directly from the inclination-controlled imbalance between λ_{dry} and λ_{wet} , rather than from any material-specific chemistry. This interpretation aligns with experimental observations of reduced wet-state longevity and intermittent reactivity on inclined metallic substrates [11,12].

Stochastic intermittency therefore represents the final element in the multiscale picture developed in this section: deterministic thinning sets rupture timing, stochastic forcing governs rewetting, and inclination biases the entire process toward rapid cycling. Together, these effects provide a leading-order basis for inclination-dependent intermittency metrics, through $\lambda_{\text{dry}}(\theta)$ and $P_{\text{wet}}(\theta)$, which directly constrain the stability, drainage and transport consequences studied in Section 5 below. In this sense, the representative crossover structure introduced in Section 3.6 complements the stochastic description by showing that the

transport and reactive transitions induced by inclination can occur within experimentally relevant angular ranges.

More detailed stochastic structure, such as long-tailed wetting intervals, state-dependent rates, or humidity-correlated transitions, falls outside the scope of the present mean-field description and constitutes a natural extension for future work.

5. Physical Consequences of the Inclination-Driven Trajectory $\Gamma(\theta)$

The dimensionless structure derived in Section 3 and the deterministic–stochastic coupling introduced in Section 4 together define a unified picture of how inclination reorganizes thin-film behavior. In particular, the inclination-driven trajectory $\Gamma(\theta)$ provides a compact organizing framework for interpreting how the governing balances evolve with geometry. Rather than acting as a secondary perturbation, inclination systematically reorders the competition among capillarity, intermolecular forces, drainage, transport, and wet-state persistence. This section extracts the main physical consequences of that trajectory, focusing on five interconnected aspects: stability, drainage and thinning, transport regimes, reactive confinement, and long-time intermittency.

5.1. Stability Regimes Under Inclination

The stability of a thin film on an inclined substrate results from the competition between capillary curvature, intermolecular interactions and the gravitational asymmetry introduced by θ . Linearising the hydrodynamic flux described in Section 2 about a uniform base state of thickness H yields the dispersion relation

$$\sigma(k) = -k^4 + \Pi'(H) k^2 + i(\text{Bo} \sin \theta) k, \quad (21)$$

where $\sigma(k)$ is the (generally complex) temporal growth rate of a Fourier mode of wavenumber k , and $\Pi'(H)$ denotes the derivative of the disjoining pressure evaluated at the base thickness. Capillarity contributes to the stabilizing term $-k^4$, intermolecular forces contribute the destabilizing term proportional to k^2 , and inclination introduces a linear drift term proportional to $i k$ that biases the disturbance toward downhill-propagating (traveling) modes rather than changing the amplification mechanism itself. Accordingly, in this leading-order formulation, inclination does not modify the growth-rate envelope but introduces a directional drift of unstable modes.

For horizontal substrates ($\theta = 0$), the spectrum is symmetric in k , and stability is determined solely by the balance between capillarity and intermolecular interactions, recovering the classical result for thin-film rupture [7,9]. This baseline behavior corresponds to the standard long-wave instability structure examined in lubrication-type studies [8]. Inclination breaks this symmetry: the additional term $(\text{Bo} \sin \theta)k$ introduces a downhill drift of unstable modes and converts symmetric dewetting patterns into traveling disturbances, while the onset of long-wave amplification remains controlled by the capillarity–disjoining balance. This effect should be interpreted as a convective bias on the propagation of disturbances, rather than a modification of the underlying amplification mechanism. As a result, perturbations with positive k (downslope) exhibit downslope propagation, while upslope modes are effectively suppressed by the convective bias. This spectral asymmetry is consistent with the directional propagation observed in experiments on inclined wetting films [12] and coating flows [4,5].

The inclination dependence of the maximum growth rate follows directly from the dispersion relation. For the growth-controlling real part, $\sigma_r(k) = -k^4 + \Pi'(H)k^2$, the most amplified mode satisfies $k_{\max} = \sqrt{\Pi'(H)/2}$ and $\sigma_{\max} = \Pi'(H)^2/4$, whereas inclination controls the corresponding drift speed through the $i(\text{Bo} \sin \theta)k$ term. Thus, in this leading-order formulation, inclination primarily changes the convective character of the instability

(propagation bias) rather than the growth-rate envelope $\sigma_r(k)$. Accordingly, changes in apparent peak position or cutoff with θ should be interpreted as schematic/illustrative unless additional θ -dependent physics enters σ_r (for instance, through a θ -dependent base state H or additional transport couplings). This separation between amplification (σ_r) and drift ($\sigma_i = (\text{Bo} \sin \theta)k$, where σ_i denotes the imaginary part of the dispersion relation associated with the inclination-induced drift) is summarized schematically in Figure 6.

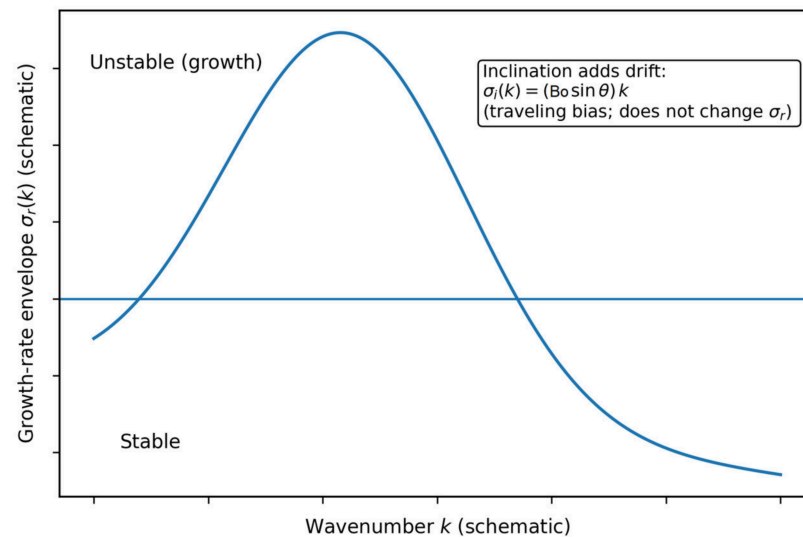


Figure 6. Schematic growth-rate envelope $\sigma_r(k)$ for a uniform base film, showing the long-wave amplification band ($\sigma_r > 0$) and the most amplified mode (peak) set by capillarity and disjoining pressure. Inclination does not modify σ_r in Equation (21) but adds a drift term $\sigma_i(k) = (\text{Bo} \sin \theta)k$ that breaks the $\theta = 0$ symmetry and biases disturbances toward downhill propagation.

Any implications for rupture pathways or spatial restructuring should therefore be understood as schematic consequences of this drift contribution, rather than direct modifications of the instability growth mechanism.

This inclination-induced convective bias in disturbance propagation establishes the foundation for the drainage, transport and reactive consequences developed in Sections 5.2–5.5 just below.

5.2. Drainage and Thinning Under Inclination

Inclination alters the drainage behavior of thin films in a systematic and theoretically transparent manner. Because the gravitationally induced flux term $\text{Bo} \sin \theta$ enters the hydrodynamic equation linearly, its influence propagates directly into the thinning kinetics of the film. This linear dependence is the same one that governs the inclination-driven coupling of the Bo , Pe and Da numbers in Section 3.5, so the drainage pathway reflects the underlying structure of the nondimensional trajectory.

For a finite film segment draining toward an edge (or a representative control volume with net outflow), the leading-order drainage law obtained from the lubrication equation reduces to

$$\partial_t h \approx -C h^3 \text{Bo} \sin \theta, \quad (22)$$

where C collects viscosity and geometric constants.

This expression encapsulates three key consequences as follows.

Accelerated thinning with inclination

Since the gravitational contribution scales as $\sin \theta$, the drainage time obeys

$$t_{\text{drain}}(\theta) \propto (\sin \theta)^{-1} \quad (23)$$

(for fixed H , L , and μ). Thus, even moderate inclination substantially shortens the film lifetime, a tendency consistent with the deterministic pathways leading to rupture discussed in Section 5.1.

This inclination dependence is the drainage counterpart of the coordinated scaling $\text{Pe} \propto \sin \theta$ appearing in the nondimensional formulation.

Enhanced sensitivity in the ultrathin regime

As the film approaches nanometric thicknesses, the cubic dependence on h makes the dynamics increasingly stiff, so that even small reductions in thickness produce disproportionately large increases in the thinning rate. Consequently, inclination-induced acceleration is magnified near the disjoining-pressure-dominated regime, making rupture markedly more abrupt than in horizontal geometries [2].

Earlier loss of continuity and reduced recovery intervals

Because evaporation competes with downhill drainage, the accelerated thinning induced by inclination shifts the balance strongly toward rupture.

Even before stochastic rewetting is considered (Section 4), the deterministic trajectory reaches the rupture threshold h_{crit} more rapidly.

The subsequent re-formed films originate from progressively thinner initial states, reinforcing the cycle of short-lived wet intervals.

Together, these drainage characteristics supply the deterministic backbone that feeds into the stochastic transitions of Section 4.

The inclination-controlled reduction of t_{drain} is therefore not a system-specific effect, but the leading-order drainage counterpart of the coordinated trajectory in the $(\text{Bo}, \text{Pe}, \text{Da})$ space derived in Section 3.

5.3. Transport Regimes: Advection, Diffusion, and Confinement

The dimensionless analysis of Section 3 showed that inclination increases the Pe number through the scaling $\text{Pe} \propto \sin \theta$.

This single geometric modification reshapes the balance between advection and diffusion within the film across three distinct regimes.

These regimes arise from the competition between downhill advection $u = q/h$ and transverse diffusion and are further modulated by the thickness-dependent confinement of ionic mobility [2,14].

The resulting geometry-induced transport regimes, and the associated crossover sequence along $\text{Pe}(\theta)$, are summarized schematically in Figure 7.

At comparably low inclination, transport is diffusion-dominated, since the advective flux remains quite weak and $\text{Pe} \ll 1$. Under these conditions, spatial concentration gradients relax faster than they are generated, so solutes remain confined within the film and their residence time is governed primarily by the local thickness and molecular diffusivity. Electrostatic confinement is strong in this regime, because double-layer overlap suppresses mobility and favors transport-limited reactions. As θ increases, the advective velocity grows proportionally to $\sin \theta$, eventually bringing the system to $\text{Pe} \sim \mathcal{O}(1)$, where a mixed advection–diffusion regime emerges. Diffusion can no longer fully eliminate the concentration gradients induced by downhill drainage, and longitudinal compositional variations, solute accumulation zones, and reaction rates coupled to the hydrodynamic timescale begin to develop. This marks the onset of geometry-induced transport asymmetry,

whereby even an otherwise nearly uniform film may preferentially carry solutes toward the downhill edge. At larger inclinations, $Pe \gg 1$ and advection becomes dominant: solutes are swept downslope faster than they can redistribute, leading to a sharp reduction in residence time. At the same time, electrostatic confinement weakens because rapid thinning (Section 5.2) drives the film below the stable-confinement regime before diffusive equilibration can occur. In this limit, the reaction dynamics are governed less by local kinetics than by the rate at which material can be supplied to, or retained within, the thinning film. The confinement window highlighted in Figure 7 therefore identifies the range of inclinations over which confinement can still persist despite the progressive increase in transport asymmetry.

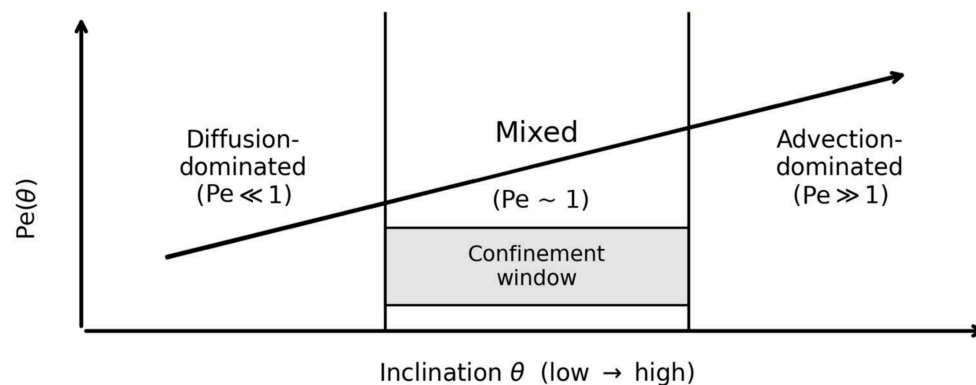


Figure 7. Schematic transport-regime sequence along inclination θ , reflecting the geometry-imposed increase in $Pe(\theta)$. As θ increases, the system crosses from diffusion-dominated ($Pe \ll 1$) to mixed ($Pe \sim 1$) and advection-dominated ($Pe \gg 1$) transport. The shaded interval (confinement window) marks the range of inclinations over which ionic mobility remains strongly confined, indicating that strong confinement and transport asymmetry can coexist over a limited parameter window.

5.4. Inclination Effects on Reactive Confinement

Although the formulation is general, electrolyte films provide a representative example of how inclination reorganizes reactive behavior.

Because the Da number satisfies

$$Da(\theta) \propto (\sin \theta)^{-1}, \quad (24)$$

increasing inclination reduces the time available for ions to remain confined within the liquid layer. This effect is reinforced by two mechanisms established in Sections 4 and 5.2: (i) the shortening of wet intervals caused by inclination-enhanced drainage and (ii) the weakening of electrostatic confinement as the film is driven rapidly into the ultrathin regime.

The combined consequence is a transition from long-residence-time, confinement-dominated behavior at relatively low inclination to comparably-short-residence-time, intermittency-limited behavior at high inclination. Reaction pathways requiring sustained connectivity—such as those involving concentrated boundary layers or strongly overlapped double layers—are progressively suppressed. Instead, reactivity becomes governed by the supply of material to the thinning film and by the stochastic occurrence of short wet intervals. These effects do not rely on electrolyte-specific chemistry: they arise generically from the reweighting of Da, Pe and the rupture rate with θ .

This inclination-driven shift in confinement and reactivity provides a physical interpretation for the reduced wet-state persistence and intermittent electrochemical activity reported experimentally on inclined metallic surfaces [11,12].

5.5. Long-Time Intermittency and Wet-State Persistence

The combined deterministic and stochastic descriptions developed in Sections 2–4 reveal a coherent and geometry-driven reorganization of thin-film behavior under inclination. As the Bo and Pe numbers increase with θ , deterministic thinning accelerates, rupture occurs earlier, and the drying pathway strengthens relative to the rewetting pathway. The stochastic model described in Section 4 shows that this imbalance raises the drying rate $\lambda_{\text{dry}}(\theta)$ while leaving λ_{wet} essentially controlled by humidity and vapor transport. The consequence is a systematic decline of the wet-state probability and a transition to highly intermittent wet/dry dynamics.

In this intermittent regime, the long-time behavior of the film is governed by sporadic and short-lived wet intervals separated by extended dry periods. The hydrodynamic structure of the film becomes increasingly asymmetric: downhill thinning accelerates with Pe, confinement breaks down earlier, and the residual film thickness approaches the rupture threshold more rapidly. Transport processes reflect the same geometric influence. At modest inclination, mixed advection–diffusion behavior persists, but at large θ the dynamics become decisively advection-dominated, with solutes swept downslope before diffusive redistribution can occur.

These inclination-induced changes have broad implications for reactive and confined films. Intermittency truncates residence times, interrupts extended reactive phases and suppresses steady confined-electrostatic regimes. The interface becomes reactive only during brief wet windows, and the corresponding reaction pathways become strongly history-dependent.

This global behavior—accelerated thinning, diminished wet-state persistence, loss of confinement, and the emergence of strong intermittency—is a generic consequence of the inclination-driven hierarchy of dimensionless groups, not of any particular chemistry.

These coupled trends predict measurable signatures: a monotonic decrease of $P_{\text{wet}}(\theta)$, a reduction in mean wet-interval duration $\langle t_W \rangle = 1/\lambda_{\text{dry}}(\theta)$, and a transition from $\text{Pe} \ll 1$ to $\text{Pe} \gg 1$ transport as θ increases.

6. Discussion

The leading-order framework developed in this paper unifies the hydrodynamic, interfacial, gravitational and stochastic mechanisms governing thin films on inclined substrates. By deriving the governing equations from first principles and studying their dimensionless structure, we have shown that inclination acts not merely as a geometric parameter but as a symmetry-breaking field that modifies drainage, stability and transport in a coordinated manner. This reorganization is encoded in a single inclination-driven trajectory in the (Bo, Pe, Da) parameter space, which emerges directly from the structure of the lubrication-type equations and is therefore only weakly dependent, at leading order, on system-specific material properties in its functional form, although the location along the trajectory remains material-dependent.

This geometric control manifests across all levels of dynamics. Deterministically, increased inclination enhances gravitational forcing, accelerates thinning, shifts instability thresholds and shortens the residence time of solutes in confined ultrathin regions. Stochastically, the strengthened drainage pathway increases the drying rate while leaving the rewetting pathway largely unaffected, thereby reducing the steady wet-state probability and enhancing the intermittency of wet/dry cycling. Together, these deterministic and stochastic consequences generate the characteristic features of inclined films: rapid thinning events, asymmetric profiles, premature loss of confinement and temporally fragmented reactive phases.

The representative parameterization introduced in Section 3.6 makes this ordering quantitatively explicit. For the illustrative ultrathin electrolyte film considered there, the reactive crossover $\theta_{\text{Da}} \approx 15.8^\circ$ precedes the transport crossover $\theta_{\text{Pe}} \approx 33.7^\circ$, while the corresponding Bond number remains far below unity. This representative example shows that substantial transport and reactive reorganization can occur even within a strongly capillary-dominated regime, and it provides a concrete quantitative anchor for the leading-order crossover structure summarized by $\Gamma(\theta)$.

Representative experimental systems reported in Refs. [11,12] appear to fall within the same region of the inclination-driven trajectory in the (Bo, Pe, Da) space, which is consistent with the leading-order scaling proposed here.

Although the formulation is general within the continuum lubrication regime, its qualitative implications are consistent with the physical conditions reported for atmospheric electrolyte films. Representative orders of magnitude, typical film thicknesses of $H \approx 10\text{--}100$ nm, lateral length scales of $L \approx 1\text{--}10$ mm, and gravitationally driven drainage velocities in the range $10^{-6}\text{--}10^{-4}$ m s $^{-1}$, all compatible with the regimes discussed in Refs. [11,12], place such systems in the low-Bond-number range ($\text{Bo} \approx 10^{-6}\text{--}10^{-4}$), with moderate-to-high Pe numbers ($\text{Pe} \approx 1\text{--}100$) and order-unity to moderately varying Da numbers. These values are broadly aligned with the inclination-dependent trends identified in Section 3, as well as with the representative crossover structure illustrated in Figure 3, supporting the physical relevance of the framework while remaining within its intended role as a leading-order, conceptual description rather than a detailed quantitative prediction.

The stochastic component of the model is deliberately minimal: the wet-to-dry and dry-to-wet transitions are treated as a two-state Poisson process with constant rates. This Markov process assumption provides a transparent mean-field description of intermittent wetting, but it does not attempt to capture heavy-tailed waiting-time distributions or humidity-driven temporal correlations. Such effects, often observed in environmental systems, may be incorporated in future work through renewal processes or continuous-time random-walk formulations.

The leading-order structure presented here also identifies several directions for further development. Extending the study to two- and three-dimensional geometries would enable the study of transverse instabilities, rivulet formation and interactions between gravitational forcing and contact-line pinning. Introducing substrate heterogeneity or patterned wettability could reveal non-trivial couplings between microscopic pinning and macroscopic symmetry breaking. Coupling the present framework to detailed electrochemical kinetic models would clarify how intermittent wetting shapes reactive pathways, especially under cyclic humidity forcing. Finally, integrating realistic stochastic humidity profiles may reproduce long-tailed wet-interval distributions observed in environmental systems.

The present paper provides a coherent physical description of thin films under geometric asymmetry, bridging hydrodynamics, intermolecular forces, confined transport and stochastic wetting within a single mathematical structure. The inclination-driven trajectory provides a compact conceptual lens through which to interpret a broad spectrum of interfacial phenomena across thin-film hydrodynamics, coating flows and related interfacial transport processes within the continuum regime.

7. Conclusions

We have developed a leading-order theoretical framework that couples hydrodynamics, intermolecular forces, gravitational asymmetry and stochastic wetting to describe the behavior of thin films on inclined substrates. The formulation, derived from first principles, identifies the key dimensionless groups governing the system and shows how inclination

systematically reweights the balance between capillarity, van der Waals forces, drainage and transport.

Inclination enhances the drying pathway without significantly affecting rewetting, leading to a monotonic reduction in wet-state persistence and the emergence of strongly intermittent wet/dry dynamics. These effects arise directly from the structure of the lubrication-type equations and the associated scalings of the Bond, Péclet and Damköhler numbers, rather than from chemistry-specific assumptions.

A representative quantitative parameterization further shows that this inclination-driven structure yields explicit crossover angles for reactive-confinement loss and transport reorganization, thereby complementing the general scaling analysis with a concrete regime illustration. In the representative case examined here, the system remains strongly capillary-dominated while still undergoing ordered Da- and Pe-controlled transitions as the inclination increases.

Although motivated by electrolyte films, the framework is general within the continuum lubrication regime and applies to confined, evaporating, deliquescent and coating films. By integrating deterministic and stochastic mechanisms within a single structure, this paper provides a coherent basis for interpreting thin-film behavior under geometric asymmetry and provides a unifying perspective on inclination-driven effects across surface-physics contexts. It also defines distinct directions for future extensions, including three-dimensional geometries, heterogeneous substrates and the coupling to fully resolved reactive models under intermittent wetting.

The aim of this study was to establish a leading-order, physically transparent theoretical structure rather than to provide fully resolved analytical or numerical solutions. The governing equations derived here enable such analyses, whether asymptotic treatments of specific drainage regimes or full numerical simulations, but these fall outside the scope of the present leading-order, system-independent framework. Future work may exploit the same formulation to obtain explicit solutions for targeted regimes or to quantify inclination effects in specific material systems.

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