Continuous and discontinuous dynamic unbinding transitions in drawn film flow

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When a plate is withdrawn from a liquid bath a coating layer is deposited whose thickness and homogeneity depend on the velocity and the wetting properties of the plate. Using a long-wave mesoscopic hydrodynamic description that incorporates wettability via a Derjaguin (disjoining) pressure we identify four qualitatively different dynamic transitions between microscopic and macroscopic coatings that are out-of-equilibrium equivalents of well known equilibrium unbinding transitions. Namely, these are continuous and discontinuous dynamic emptying transitions and discontinuous and continuous dynamic wetting transitions. We uncover several features that have no equivalent at equilibrium.

The equilibrium and non-equilibrium behaviour of mesoscopic and macroscopic drops, menisci and films of liquid in contact with static or moving substrates is not only of fundamental interest but also crucial for a large number of modern technologies. On the one hand, the equilibrium behaviour of films, drops and menisci is studied by means of statistical physics. A rich substrate-induced phase transition description that incorporates wettability via a Derjaguin (disjoining) pressure we identify four qualitatively different dynamic transitions between microscopic and macroscopic coatings that are out-of-equilibrium equivalents of well known equilibrium unbinding transitions. Namely, these are continuous and discontinuous dynamic emptying transitions and discontinuous and continuous dynamic wetting transitions. We uncover several features that have no equivalent at equilibrium.

On the other hand, it is a classical hydrodynamic problem to study how droplets slide down an incline [3–6], how moving contact lines (where solid, gas and liquid meet) develop sawtooth shapes at high speeds [6–8], or how the free surface of a bath is deformed when a plate is drawn out, as sketched in Fig. 1(a). Early on it was reported that for sufficiently large plate velocities $U$ a homogeneous macroscopic liquid layer is deposited on the drawn plate [Fig. 1(d)]. The resulting coating layer is called a Landau-Levich film. Far away from the bath it has a thickness $h_{\infty}$ that depends on the capillary number $Ca = \eta U / \gamma$ through the power law $h_{\infty} \propto Ca^{n/3}$ [9] where $\eta$ and $\gamma$ are the viscosity and surface tension of the liquid, respectively. This coating technique is widely used and became a paradigm for theoretical (e.g., [6, 9–12]) and experimental (e.g., [13–17]) studies.

In contrast, at very low plate velocities $U$ no macroscopic film is drawn out but a deformed steady meniscus coexists with the dry plate far away from the bath [8, 16, 18–20] [Fig. 1(b)]. This meniscus only exists for capillary numbers smaller than a critical one, i.e., $Ca < Ca_c$ [18]. Close to $Ca_c$ the meniscus develops a foot of a length $L_f$ [Fig. 1(c)] that diverges at $Ca_c$, either continuously [21] or discontinuously [19]. As the steady free surface meniscus coexists with the dry moving plate, there exists a receding three-phase contact line whose best description is still debated (see, e.g., [1, 22, 23]).

Previous works [18, 19, 21] employ a slip model that allows the film height to go to zero at the contact line and avoids the contact line singularity through the slip [1]. Although, a slip model allows for a quantitative study of meniscus solutions and Landau-Levich films, it is not able to describe transitions between them as in a slip model they are topologically different [cf. Figs. 1(b) and (c) vs. Fig. 1(d)]. Note that this concerns the actual transition dynamics as well as the description of transitions in dependence of control parameters such as the plate speed.

In contrast, here we employ a long-wave mesoscopic hydrodynamic model that describes wettability via a Derjaguin (disjoining) pressure, i.e., a precursor film model. An investigation of the non-equilibrium transitions between meniscus solutions and Landau-Levich films then allows for an identification of four qualitatively different dynamic unbinding transitions, namely, continuous and discontinuous dynamic emptying transitions and discontinuous and continuous dynamic wetting transitions.
wetting transitions. Note that far from the transition regions, the predictions of precursor and slip models agree very well and can be quantitatively mapped [24].

In particular, to describe the meniscus and the film dynamics we use the following non-dimensionalised [25] evolution equation for the film thickness profile \( h(x, t) \) [22, 26, 27]:

\[
\frac{\partial h}{\partial t} = -\partial_x \left[ h^3 \partial_x \left( \frac{\partial^2 h}{\partial x^2} + \Pi(h) \right) \right] - h^3 G(\partial_x h - \alpha) - U h,
\]

that may be derived as long-wave approximation of the Navier-Stokes and continuity equations with no-slip boundary conditions at the liquid-solid interface and kinematic and stress balance conditions at the liquid-gas interface [28]. Here \( U \), \( G \) and \( \alpha \) are the scaled plate velocity (Capillary number), gravity (Bond number), and inclination angle of the plate, respectively [25]. The wettability of the partially wetting liquid is described via the Derjaguin (or disjoining) pressure \([29]\)

\[
\Pi = -\frac{1}{h^3} \left( 1 - \frac{1}{h^2} \right),
\]

derived in Ref. [30] from a modified Lennard-Jones potential with hard-core repulsion, see [25]. The disjoining pressure is related to a wetting or adhesion energy \( f(h) \) via \( \Pi = -df/dh \).

It should be noted that the hydrodynamic long-wave model, Eq. (1) with Eq. (2), directly corresponds to a gradient dynamics of an underlying interface Hamiltonian (or free energy)

\[
F[h] = \int \left[ \xi \gamma + f(h) \right] dx
\]
as often used to study the above introduced equilibrium unbinding transitions [31]. This equivalence allows for a natural understanding of the various occurring transitions as non-equilibrium (or dynamic) unbinding transitions (see below).

To calculate steady film and meniscus profiles one sets \( \partial_t h = 0 \), then integrates Eq. (1) once and solves the resulting three-dimensional dynamical system in \( (h, \partial_x h, \partial_x^2 h) \) with appropriate boundary conditions: (i) far from the bath for \( x \to -\infty \) one imposes that the film profile approaches a flat film of unknown height \( h_\infty \) that is determined as part of the solution while (ii) the approach towards the bath for \( x \to \infty \) is described by an asymptotic series that can be rigorously derived via a center manifold reduction [33]. Steady profiles and bifurcation diagrams are numerically obtained employing pseudo-arclength continuation [34]. The employed main solution measure is the dynamic excess volume \( \Delta V \equiv V - V_0 \) with \( V = \int \left( h(x) - h_\infty \right)dx \), where \( V_0 \) is \( V \) at \( U = 0 \). Note that for solutions with a long protruding foot-like structure \( \Delta V \) is approximately proportional to the length of the foot [35].

An analysis of the changes that steady menisci undergo with increasing plate speed \( U \) shows that four qualitatively different cases exist depending on the plate inclination angle \( \alpha \). Each case is related to a distinguished nonequilibrium unbinding transition as illustrated in Fig. 2 that shows for all four cases typical bifurcation diagrams in dependence on \( U \) and steady height profiles for selected values of \( U \):

(a) At small \( \alpha \), the volume \( \Delta V \) monotonically increases: first slowly, then faster until it diverges at about \( U_\infty \approx 0.04 \) [Fig. 2(a)]. The corresponding simple meniscus profiles first

![Bifurcation curves indicating the occurrence of qualitatively different behaviour with increasing plate inclination angles](image-url)

![Advancing and receding foot-like structures](image-url)

FIG. 2: Bifurcation curves indicating the occurrence of qualitatively different behaviour with increasing plate inclination angles (a) \( \alpha = 0.1 \), (b) \( \alpha = 1 \), (c) \( \alpha = 3 \), and (d) \( \alpha = 10 \). The main panels show the excess volume \( \Delta V \) over domain size \( L \) (see main text) in dependence of the plate velocity \( U \), while the respective insets give Log-normal representations of steady film profiles at selected plate velocities as indicated by corresponding labels at the profiles and at the bifurcation curves. Additionally, panels (c) and (d) give a film profile at \( U = 3 \). The domain size is \( L = 1000 \). Arrows indicate how the profiles change as one moves along the bifurcation curves.

FIG. 3: (a) Advancing and receding foot-like structures are characterized by the dependence of the velocity \( V_F \) of the front that connects the ultrathin coating layer of thickness \( h_\infty \) with the foot plateau of height \( h_{foot} \) on the velocity difference \( \alpha = U - U_{\infty} \) where \( U_{\infty} \) changes with the plate inclination \( \alpha \). Note that the curves for various \( \alpha \) as given in the legend collapse onto a master curve, indeed \( V_F \approx U - U_{\infty} \). Panels (b) and (c) give for \( \alpha = 0.5 \) space-time plots representing the time evolution [32] of a receding and an advancing foot, respectively, at values of \( U \) indicated by small letters in panel (a). The evolution in (b) converges to a steady simple meniscus, while in (c) the foot advances with constant speed until its tip reaches the domain boundary. Then at \( \tau \approx 4 \) the foot transforms into a Landau-Levich film of a different thickness via a fast shallow backwards-moving front.
deform only slightly due to viscous bending before a distinguished foot-like protrusion of a height $h_{\text{foot}} \approx 10$ develops whose length $L_{\text{foot}}$ diverges $\propto \ln[(U_{\infty} - U)/U_{\infty}]^{-1}$. This corresponds to a continuous dynamic emptying transition, a dynamic analogue of the equilibrium transition discussed in Ref. [2]. One may also say that at $U_{\infty}$ the tip of the foot unbinds from the bath. For $U > U_{\infty}$ the foot advances with a constant velocity $V_F \approx (U - U_{\infty})$ as shown in Fig. 3.

(b) Above a first critical $\alpha = \alpha_1 \approx 0.103$, the transition changes its character and becomes a discontinuous dynamic emptying transition that has no analogue at equilibrium. As shown in Fig. 2(b), $\Delta V$ increases first monotonically with $U$ until a saddle-node bifurcation is reached at $U_1$ where the curve folds back. Following the curve further, one finds that it folds again at $U_2$. This back and forth folding infinitely continues at $U_{\infty}$ that exponentially approach $U_{\infty}$ from both sides and that separate linearly stable and unstable parts of the solution branch. This exponential (or collapsed) snapping has no analogue at equilibrium. Instead of a protruding foot of increasing length that unbinds from the meniscus one finds a hysteretic transition [in Fig. 2(c) between $U = 0.1$ and 0.3] towards a coating layer whose thickness homogeneously increases with increasing $U$, i.e., the layer surface unbinds from the substrate in a discontinuous dynamic wetting transition.

(d) With increasing $\alpha$ the hysteresis of the discontinuous transition becomes smaller until at a third critical $\alpha = \alpha_3 \approx 5.92$ the two saddle-node bifurcations annihilate in a hysteresis that further illustrated in Fig. 4. For all $\alpha > \alpha_3$ one finds a continuous dynamic wetting transition. As in both cases - (c) and (d) - at large $U$ the coating layer thickness follows the power law $h_{\infty} \propto U_{\infty}^{2/3}$, we identify these unbinding states as Landau-Levich films [9]. The critical velocity where the transition between the microscopic and macroscopic layer occurs, scales as $\alpha^{3/2}$.

Note that the dynamic emptying transitions of cases (a) and (b) and the crossover between them is also observed employing a slip model [19, 21]. However, as normally slip models do not take account of the mesoscale wetting behaviour they are unable to describe the discontinuous and continuous dynamic wetting transitions of cases (c) and (d), respectively, as these represent transitions between the topologically different meniscus and film solutions.

To summarize our findings we present in Fig. 5 a phase diagram in the $(U, \alpha)$ parameter plane allows us to identify regions of different behaviour that are limited by the loci of (i) saddle-node bifurcations of steady film surface profiles (black solid lines) and (ii) by the dependence of the limiting velocity $U_{\infty}$ on $\alpha$ (blue dotted line). The existence of an additional solution family close to $U_{\infty}$ in region (c) is indicated by a grey shading. The behaviour in regions (a) to (d) is described in the main text.
$U_0 > U > U_\infty$ there is always a maximal stable foot length $L_{\text{max}}^-$ towards which a longer foot will retract. For each $U$ with $U_\infty > U > U_1$ there is always a maximal unstable steady foot length $L_{\text{max}}^+$ beyond which the foot will prolongate continuously. $L_{\text{max}}^+ [U_{\text{max}}^+]$ logarithmically diverges as $U$ approaches $U_\infty$ from below [above].

In region (c), i.e., for $\alpha_2 < \alpha < \alpha_3$, the lines of saddle-node bifurcations limit a region where initial conditions decide whether an ultrathin layer or a macroscopic Landau-Levich coating is obtained. Below [above] the hysteresis range one only finds the ultrathin [Landau-Levich] coating. In region (d), i.e., for $\alpha_3 < \alpha$, the change between the two coating types is continuous.

Although an extended analysis of the characteristics of the observed qualitative changes with increasing inclination angle is beyond our present scope, we highlight some further important facts. The crossover between regions (a) and (b) at $\alpha = \alpha_1$ can be understood in terms of a change of the character of the spatial eigenvalues (EV) of a flat film of a height that corresponds to the foot height [21, 33]: In region (a) all EV are real while in region (b) only one is real and the other two are a pair of complex conjugate EV. The crossover between regions (c) and (d) at $\alpha = \alpha_3$ results from a hysteresis bifurcation where two saddle-node bifurcations annihilate. However, the crossover between regions (b) and (c) at $\alpha = \alpha_2$ that results in the strongest qualitative change, namely, from a dynamic emptying to a dynamic wetting transition cannot be understood by analysing a single family of steady profiles. As illustrated in Fig. 6 the crossover results from a reconnection (reverse necking bifurcation) at $\alpha = \alpha_2$ that involves two solution families. Both continue to exist on both sides of $\alpha_2$. This results in intricate behaviour in certain small bands of the $(U, \alpha)$ plane and, in particular, around $\alpha_2$ that will be studied in more depth elsewhere. For instance, in the fine grey band around $U_\infty$ in region (c) [Fig. 5], there exist various stable extended meniscus profiles. They correspond to the left branch in Fig. 6(b). Experimentally, they might only be obtained through a careful control of the set-up at specific initial conditions.

To conclude, we have shown that a long-wave mesoscopic hydrodynamic description of the coating problem for a plate that is drawn from a bath allows one to identify and analyze several qualitative transitions if wettability is modelled via a Derjaguin pressure, i.e., with a precursor film model. As a result we have distinguished four regions where different dynamic unbinding transitions occur, namely continuous and discontinuous dynamic emptying transitions and discontinuous and continuous dynamic wetting transitions. These dynamic transitions are out-of-equilibrium equivalents of well-known equilibrium emptying and wetting transitions. Beside features known from the equilibrium versions, our analysis has uncovered several important features that have no equivalents at equilibrium. A future study of the influence of fluctuations might allow one to answer the question which surface profile is selected in the multistable regions.

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