Exponentially fast Thinning of Nanoscale Films by Turbulent Mixing

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Films are nanoscopic elements of foams, emulsions and suspensions, and form a paradigm for nanochannel transport that eventually tests the limits of hydrodynamic descriptions. Here, we study the collapse of a freestanding film to its equilibrium. The generation of nanoscale films usually is a slow linear process; using thermal forcing we find unprecedented dynamics with exponentially fast thinning. The complex interplay of thermal convection, interface and gravitational forces yields optimal turbulent mixing and transport. Domains of collapsed film are generated, elongated and convected in a beautiful display of chaotic mixing. With a timescale analysis we identify mixing as the dominant dynamical process responsible for exponential thinning.

In nature, thin liquid films form the interfaces in foams, emulsions, or they sheath solid particles in a liquid environment. Currently, interest in thin films is driven by science, but also by technological demands, since they are the basic structural elements of dispersed systems, separating gas bubbles in foams, droplets in emulsions, or they sheath solid particles in a liquid environment. Currently, interest in thin films is driven by science, but also by technological demands, since they are the basic structural elements of dispersed systems, separating gas bubbles in foams, droplets in emulsions, or they sheath solid particles in a liquid environment.

Thin film dynamics is governed by gravitational, capillary or interfacial forces, inducing the existence of the disjoining pressure. The latter combines long- and short-range molecular forces: electrostatic, van der Waals (vdW), and steric forces and strongly depends on the distance between the interacting surfaces. Whereas films on substrates are established in industry and research, freestanding thin liquid films still provide a challenge in experiments and theory alike. Consequently, the study of foam films is of central interest e.g. [4-7]. We contribute by presenting a novel approach to thinning of vertically oriented, freestanding, thermally forced, nonequilibrium foam films.

As a result of the force balance two stable equilibria may occur, depending on the chemical composition of bulk solution and chosen surface active agents (surfactants): Common Black Films with a thickness of more than 10 nm are formed when electrostatic interactions balance the dominant van der Waals force, and, of course, gravity and capillarity [1,2]. Newton Black Films are stable with a thickness of less than 10 nm, due to repulsive short range steric forces and strongly depends on the distance between the interacting surfaces. Whereas films on substrates are established in industry and research, freestanding thin liquid films still provide a challenge in experiments and theory alike. Consequently, the study of foam films is of central interest e.g. [4-7]. We contribute by presenting a novel approach to thinning of vertically oriented, freestanding, thermally forced, nonequilibrium foam films.

In a foam film, the downward motion of the BF front is at constant velocity, limited by the thin film bulk velocity which follows a Poiseuille flow [12]. The drainage, steady-state profile and thermal effects have been predicted earlier, experiments with evaporation and comparatively uncontrolled chemistry [13,14] suggest an exponential decrease in thinning speed.

Here, a foam film is brought far into nonequilibrium by pointlike thermal forcing, cf. Fig. 1 b. The additional force counteracts gravitation and capillarity, and changes the dynamics from linear to exponential. After a transient period, a global convective flow with complex dynamic behavior is established, marked by two-dimensional turbulent mixing combined with surface instabilities. Image recording allows for a characterization of the flow field, global mixing properties, and eventually the thinning law, as the film progresses towards a global BF state. As it turns out, the observed behavior is only possible by a complex interplay of various dynamical processes within the nanoscale film.

Experiment
The experimental setup consists of a vertical rectangular aluminium frame with rounded corners, 45 × 20 mm, enclosed by an atmosphere-preserving cell with a glass window for video recording, cf. Fig. 1 more details and video, see [15]. Both Common and Newton Black Film are optically transparent, and show only a subtle difference in reflectivity which is not resolved by our setup. For the set conditions it is expected that a Newton Black Film forms, however it will be referred to with the general term black film (BF). Thermal forcing is effected by inserting a cooled copper needle at the film center (T = −169°C). The needle enters the cell through a fitting hole, centred on the thin film area. Ambient temperature was constant at 20°C, with a Rayleigh number Ra ≈ 107, typical for turbulence.

The solution from which the liquid film was drawn con-
Foam film in aluminium frame - thinning without thermal forcing. a: Foam film in aluminium frame - thinning without thermal forcing. b: Perspective view. A: Light source, B: diffuser screen, C: video camera, D: casing to prevent evaporation, with plexiglass window, E: BF area F: Cooling copper needle at \(-169^\circ\)C, G: Soap reservoir, H: Aluminium frame. The convective pattern, established with thermal forcing is sketched, along with the BF and the thick, wedge-like region. The latter decreases in the course of time. c: Foam film in aluminium frame - thinning with thermal forcing. The convection rolls are in the lower half of the frame, above the cold needle a stably stratified region has formed.

We clearly observe a linear behavior with constant velocity \(v_{\text{regular}} \approx 18 \mu m/s\), in accordance with \[12\]. The very first quantitative thinning experiments \[14\] reported an exponential slowing down. This can most likely be attributed to uncontrolled evaporation from the film since the atmosphere was not saturated, already anticipated by Mysels\[14\]. For the aspect ratio here (3:5), the main flow is through the Plateau border, as explained above.

With thermal forcing ((A) in Fig. 2 and Fig. 3), the film is cooled down rapidly in the center and a small, frozen region appears surrounding the needle. Thermal energy is exchanged at its boundaries and heavy convection starts. A weakly turbulent flow is rapidly established with 2 symmetric, dominant eddies, cf. Fig. 2 c. As a result of this convection, two different regimes are observed: a first regime with faster, but still linear thinning, and a second regime with exponential thinning.

In the linear regime (150 s – 277 s) the velocity of the BF front is still constant, however the magnitude is increased by a factor of 3 to \(v_1 = 66 \mu m/s\) (cf. Fig. 3 blue line). The enhancement is explained as follows:

Fluid is transported by convection vertically from top to bottom, however the outflow into the reservoir is slower than convection. Necessarily a vertical upflow at the left and right boundary is generated. This in turn causes a suction of fluid from the bottom. This results in faster uniform motion of the BF front, whose speed is now determined by the net deposition rate of fluid through the bottom meniscus and subsequent outflow from the same, and is no longer limited by the flow through the vertical menisci. The latter is enhanced by the more constant thickness of the film (with height) resulting in the increased velocity.

The second, exponential regime starts at \(t \approx 277 s\) (B in Fig. 2), its dynamics is explained as follows: The BF spots rise spontaneously due to thermal and mechanical fluctuations, and are subsequently transported around by the convection. A BF spot is basically a domain of BF (5–20 nm) surrounded by much thicker film (100–1000 nm). This BF spot can only grow by transporting liquid away from the spot through the surrounding film. Hence, this must take place under Poiseuille flow conditions, due to the nanoscale thickness of the film. Due to gravity, a BF spot lifts up, like a bubble.

Due to convection, the growth of BF spots is affected by the shear stress at their interface. Beyond a certain threshold of size and speed (approx. 285 s, see also \[15\]) the BF spots are stretched, leaving behind a thin BF filament. These filaments are folded and seed i) new spots acting as multipliers, ii) “droplets” of thick film within the BF spots. Consequently two additional flows are established: BF spots are lifted to the top to join the BF area, droplets descend due to gravity and eventually flow out into the bottom reservoir. The droplets appear in a grey color since their reflection is diffuse, (cf. Fig. 2 285 s). These processes can only take place when the BF spots (droplets) are light (heavy) enough to escape the
convection roll. The transport of the droplets is much faster than Poiseuille flow permits, and the exact motion is therefore difficult to describe analytically.

Let us comparing the dominant timescales for thinning with and without thermal forcing. Essentially, the thickness varies due to i) density variation according to the local temperature; this effect is of the order $\Delta \rho / \Delta T \rho_0 \approx 0.005$ ii) advection of $h$ with a ratio 5/500 (final vs. initial thickness).

This thinning process is multiplicative and effectively obeys an exponential decrease of the transient, thick phase: $A = \gamma (A_0 - A)$, with $A$ the area covered by thick film, a time constant $\tau = 1/\gamma$ and a thinning speed $v \approx A/L_y$ with $L_y$ the lateral extension of the film. Space directions are as indicated in Fig. 1 b. The thinning timescale is then $\tau$ which is measured to be $\tau = 4.76 \text{s}$, a thinning process which is 500 times faster than usual!

In general, the timescale depends on geometry and flow properties and enters parametrically into $\tau(\nu, h, L_x, L_y)$. To obtain an estimate, consider $V = \int_{A_0} dx dy \ h(x,y)$, where $A_0 = L_x \cdot L_y$ is the total area. The area-averaged growth speed is given in the most unstable, varicose mode \cite{2}.

$$V = \int_{A_0} dx dy \ \bar{h} = - \int_{A_0} dx dy \ h(x,y) \nabla_2 u(x,y) \quad (1)$$

with $\nabla_2$ the two dimensional divergence and $u$ the corresponding velocity field. Note that i) $\bar{h}$ is the convective time derivative, i.e. the local growth and ii) the flow is highly compressible in 2D, justifying the above equation.

On average, as denoted by brackets, the local thickness becomes $\bar{h} = - h \langle \nabla_2 u \rangle$ \cite{19}, which is coupled to a complicated equation for the velocity.

The flow is dominated by two local structures, the BF spots and the BF channels. Both expand and thus $\langle \nabla_2 u \rangle$ is larger than zero, i.e. the thickness $h$ decreases exponentially. In the absence of a restoring force, this would lead to rupture; in this case the divergence of the velocity converges to zero for the thickness going to its equilibrium BF value. However, if the thickness decreases in one area, there must be a corresponding increase in nearby regions, leading to “rims”, similar to the ones found in evaporative dewetting \cite{19}. They are also subject to gravitation, and fluid flows to the bottom. The time scale is now set by the convection in contrast to the Poiseuille flow for the unforced case.
This can be tested by calculating the time scales of the involved processes: thermal forcing, gravitation, steric and electrical forces (including Van der Waals), capillarity, mechanical strain (dissipation). To estimate the important effects, we calculate Rayleigh-, Capillary-, Marangoni-, Biot-, and Prandtl numbers ($Ra$, $Ca$, $Ma$, $B$, $Pr$), and the dimensionless Hamaker constant $A$. This leads to the following values: $Ra \sim 10^7$, $Pr \sim 7$, $Ma \sim 10^3$, $B \sim 10^{-3}$, $A \sim 10^{-4}$, from which we deduce that the dominant force is thermal. The convective time scale is calculated by the characteristic turnover time $\tau_{\text{turn}} \sim \frac{2L}{u} \sim 5 \text{ s}$. Eventually, the time scale of the strain, $\tau_{\text{strain}} \sim 0.4 \text{ s}$, responsible for the local generation of BF spots. It is smaller than the convective one, consequently convection rules the exponential decrease of thick film. The measured time constant $\tau = 4.76$ coincides perfectly with the convective time scale, given the roughness of our assumptions and the complexity of the process.

To produce a local BF spot, the surfactants must fluctuate very rapidly such that a hole cannot be filled immediately from the bulk excess concentration. Stretching and folding: from the local strain rate $\tau_{\text{strain}}$, the mixing efficiency, is $E = 0.075$, is calculated. Folding is related to the intersection of stable and unstable manifolds, which in our experiment are time dependent. The time-averaged flow has two hyperbolic points, which are heteroclinically connected, providing a basis for a horsehoe providing the folding.

**Discussion** We have demonstrated the dramatic acceleration of the thinning of a foam film by thermal forcing. We use novel experimental techniques to control the properties of the thin liquid film in a precise manner, i.e. a measurement chamber that inhibits evaporation from the film surface. The analysis of the fluid flow is local and global, by tracking BF spots to measure local stretching, folding and global thinning rate.

The thermal driving leads to convection, which changes the dynamics of thinning from linear to exponential. This is not only substantially faster, but qualitatively different from the classical, thermally homogeneous, thinning process. This result can be explained: the growth of black film area is driven by the pressure gradient at the interface with the non-equilibrium phase. Thus the interface length determines the overall thinning rate. By advection and stretching of black film spots, trails are left behind which increase multiplicatively the interface length resulting in the exponential thinning behaviour. Efficient transport and filamentation are guaranteed by the mixing properties of the flow.

We plan to widen our work to a Rayleigh-Bénard setup where the influence of interfacial forces can be studied, or, more technically, in a controlled mixing of substances in a quasi 2D setup. Further, with chemical control one can tune the film thickness and thereby observe the dependence of thermodynamical and hydrodynamical properties on the thickness, eventually testing the limits of continuum description. A comparison with quantum calculations will be a formidable task for future research.

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[1] B. Derjaguin, *Theory of stability of colloids and thin films* (Consultants Bureau New York and London, 1989).
[2] A. Oron, S. H. Davis, and S. G. Bankoff, Rev. Mod. Phys. 69, 931 (1997), nice review on the fluid properties in thin liquid films.
[3] G. Reiter, Science 282, 888 (1998).
[4] H. Kellay, Nature Physics 7, 279 (2011).
[5] H. Kellay, X. Wu, and W. Goldburg, Physical Review Letters 74, 3975 (1995).
[6] E. Prud’homme R. K., Khan S. A., *Foams: Theory, Measurements, and Applications* (Dekker, N.Y., 1996).
[7] D. Exerowa and P. Kruglyakov, *Foam and foam films: theory, experiment, application* (Elsevier, New York, 1998).
[8] E. J. W. Verwey and J. T. G. Overbeek, *The Theory of the Stability of Lipophobic Colloids* (Elsevier, Amsterdam, 1948).
[9] M. Jones, K. Mysels, and P. Scholten, Transactions of the Faraday Society 62, 1336 (1966).
[10] J. Israelachvili, *Intermolecular and surface forces* (Academic press London, 1991).
[11] H. Stein, Advances in Colloid and Interface Science 34, 175 (1991).
[12] S. Stoyanov, V. Paunov, E. Basheva, I. Ivanov, A. Mehrteab, and G. Broze, Langmuir 13, 1400 (1997).
[13] R. Bruinsma, Physica A Statistical Mechanics and its Applications 216, 59 (1995).
[14] K. Mysels, S. Frankel, and K. Shinoda, *Soap films: studies of their thinning and a bibliography* (Pergamon Press, 1959).
[15] M. Winkler, G. Kofoed, R. Krastev, and M. Abel, *Superfast thinning of a nanoscale thin liquid film* (2011), video resource, URL: [http://arxiv.org/abs/1110.3377](http://arxiv.org/abs/1110.3377)
[16] S. Stöckle, P. Bleuca, H. Mahwald, and R. Krastev, Langmuir 26 (7), 4974 (2010).
[17] M. Winkler and M. Abel, in *Particles in Turbulence 2011*, edited by M. Abel, E. Bodenschatz, and F. Toschi (AIP, Melville, NY, 2011), accepted.
[18] Y. Couder, J. Chomaz, and M. Rabaud, Physica D 37, 384 (1989).
[19] H. Diamant and O. Agam, Physical Review Letters 104, 47801 (2010).
[20] J. Ottino, *The kinematics of mixing: stretching, chaos, and transport* (Cambridge Univ Pr, 1989).