Air Entrainment by Viscous Contact Lines

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The entrainment of air by advancing contact lines is studied by plunging a solid plate into a very viscous liquid. Above a threshold velocity, we observe the formation of an extended air film, typically 10 microns thick, which subsequently decays into air bubbles. Exploring a large range of viscous liquids, we find an unexpectedly weak dependence of entrainment speed on liquid viscosity, pointing towards a crucial role of the flow inside the air film. This induces a striking asymmetry between wetting and dewetting: while the breakup of the air film strongly resembles the dewetting of a liquid film, the wetting speeds are larger by orders of magnitude.

Objects that impact on a liquid interface can entrain small bubbles of air into the liquid. This happens for example when raindrops fall in the ocean\textsuperscript{1} or when liquid is poured into a reservoir at sufficiently large speeds\textsuperscript{2,3}. Such entrainment of air is often a limiting factor in industrial applications such as coating and nano-scale printing techniques, where the bubbles disturb the process\textsuperscript{4,5}.

A well studied case is the entrainment of air by very viscous jets impacting on a reservoir of the same liquid\textsuperscript{2,3,6,7}. The onset of entrainment is essentially determined by the properties of the liquid, $U_e \sim \gamma/\eta_l$, which reflects a balance of the liquid viscosity $\eta_l$ and the surface tension $\gamma$. Changing the nature of the gas only has a minor influence on the entrainment process\textsuperscript{2,3}.

A very different picture has emerged recently in the context of drops impacting on a wall, for which the presence of air has a dramatic effect\textsuperscript{8–10}. It was found that splashing can be suppressed completely by reducing the air pressure to about a third of the atmospheric pressure. This caused huge excitement, in particular because such a pressure reduction does not lead to any change of the gas viscosity $\eta_g$\textsuperscript{11–13}; pressure only affects the gas density, and thus the speed of sound and the mean free path in the gas. A similar paradox is encountered for air entrainment by rapidly advancing contact lines, where a liquid advances over a surface that it partially wets\textsuperscript{2,4,14–18}. Once again, it was found that depressurizing the gas leads to a significant increase of the threshold of air entrainment\textsuperscript{18,19}. This contradicts the classical viewpoint that, for given wettability, the contact line speed depends mainly on the liquid properties as $\sim \gamma/\eta_l$\textsuperscript{14,20–22}, with minor influence of the gaseous phase.

In this Letter we reveal the role of the air for advancing contact lines in a paradigmatic system: a partially wetting solid plate is plunged into a reservoir of viscous liquid (Fig. 1). At sufficiently high speeds we observe the entrainment of an air film, typically 10 microns thickness, which subsequently decays into bubbles. The liquid viscosity $\eta_l$ is varied over more than two decades by using silicon oils of different molecular weights. It is found that the entrainment speed $U_e$ changes much less than the expected scaling $\sim 1/\eta_l$. Using an approximate hydrodynamic model we argue that this can be attributed to the flow of air into the strongly confined film, making the contact line velocity strongly dependent on both

\begin{figure}[h]
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\includegraphics[width=\textwidth]{fig1}
\caption{Air entrainment by a contact line when a solid plate is plunged into a viscous liquid. (a,b) Sketch of dynamical meniscus below the threshold of air entrainment (a), and above the threshold of air entrainment (b). In the latter case a film of thickness $h$ is formed. (c,d) Experimental images of the entrained air film in silicone oils of varying viscosity $\eta_l$. (c) For $\eta_l = 0.1$ Pa s, an extended air film is entrained behind the contact line moving downwards into the bath. The film is destroyed by the formation of “rewetting” holes. The diagonal dark line is the reflection of a straight wire that gives an impression of the interface profile. (d) For a more viscous oil, $\eta_l = 5$ Pa s, the entrained air film is rapidly destabilized to form small bubbles (dark spots).}
\end{figure}
gas and liquid viscosities. This induces a striking asymmetry between wetting and dewetting: the same liquid can advance much faster than it recedes, by orders of magnitude.

The experiments are carried using silicon oils (PDMS, Rhodorsil 47V series) with dynamic viscosities \( \eta = 0.02, 0.10, 0.5, 1.0 \) and 5 Pa.s. These liquids are essentially non-volatile, insensitive to contamination, while the surface tension \( \gamma = 22 \text{ mN.m}^{-1} \) and density \( \rho = 980 \text{ kg.m}^{-3} \) are approximately constant for all viscosities.

The reservoir is a transparent acrylic container of size is 29x15x13.5 cm, which is much larger than the capillary length \( \ell_c = (\gamma/\rho g)^{1/2} = 1.5 \text{ mm} \). The substrate consists of a silicon wafer (circular, diameter 10 cm), which is coated by a thin layer of fluorinated material (FC 725 (3M) in ethyl acetate). For all liquids, this results into static contact angles between 51° and 57°. The wafer is clamped onto a 10 mm thick metallic blade screwed to a 50 cm long high-speed linear stage. The combination of using controlled speeds and very viscous liquids one avoids complexities of splashing as well as the formation of interface cusps \[4, 14, 16–18\]. In addition, the effect of inertia is eliminated both in the gas and in the liquid; the relevant Reynolds numbers are at worst \( \Re \approx 1 \) for very extended air films (Fig. 1c). At the front of the film, the contact line develops a ridge-like structure that is common for dewetting of liquid films \[23, 25\]. The peculiarity of the present experiment is that in this case the air is dewetted, not the liquid.

An even more striking analogy with classical dewetting of liquids is the nucleation of nearly circular regions inside the film (Fig. 1). However, the circles now represent regions of rewetting, where the liquid reestablishes the contact with the solid. These “rewetting holes” can be considered as the inverse of the “dewetting holes”, since the roles of air and liquid are exchanged. Figure 2a shows a close-up of a rewetting hole (cross-section sketched in Fig. 2b). The radius of the holes increases linearly with time, and the advancing contact lines collects the air inside a thick rim. While this is analogous to the inverse problem of the dewetting holes (Fig. 2d), the process is by no means symmetric: the rewetting holes grow with a velocity \( U_e \) that is orders of magnitude faster than their dewetting counterparts, up to a factor 1000 for the liquids used in this study.

We further quantify the velocity of air entrainment for different liquid viscosities. A first measurement of \( U_e \) is obtained from the growth velocities of the rewetting holes as in Fig. 2. A second entrainment velocity can be extracted by a selecting a central part of the front of the air film, for which we obtain the contact line velocity \( U_{cl} \) in the frame of the liquid reservoir. Figure 3 reports the measured values for \( \eta = 0.1 \text{ Pa.s} \), showing that the contact line velocity increases linearly with plate velocity \( U_p \). Interestingly, however, the relative velocity,
The key result of the velocity measurements is that, although $U_c$ decreases with liquid viscosity, the dependence $U_p - U_{cl}$ turns out to be independent of the plate velocity $U_p$, for $\eta_l=0.1\text{Pa.s}$. The relative velocity $U_p - U_c$ (circles) is independent of the plate speed. (b) Entrainment speed $U_e$ for different liquid viscosities $\eta_l$, measured in two ways: the circles represent the relative velocity with respect to the plate, $U_p - U_{cl}$, while the triangles are the rewetting speeds of the holes as in Fig. 2. (c) Film thickness $h$ for different $\eta_l$, taken at constant plate velocity $U_p = 0.67 \text{m.s}^{-1}$. The open circle was taken for a liquid jet of glycerol entraining air at the same speed.

$U_p - U_{cl}$, turns out to be independent of the plate velocity and therefore seems to be an intrinsic property of the advancing contact line. This is why we may consider the growth velocity of the rewetting holes to be an independent measurement of the entrainment velocity. The resulting entrainment velocities $U_e$ are shown in Fig. 3b, as a function of liquid viscosity $\eta_l$. Indeed, the two experimental definitions of $U_e$ agree very well for the smallest $\eta_l$ (closed circles are based on the front of the film, open triangles correspond to rewetting holes). For larger $\eta_l$, the film rapidly destabilizes and it is more difficult to define the front of the film. This induces a difference between the two types of velocity measurements of about a factor 2; the hole velocities are certainly more reproducible in this very viscous regime.

The key result of the velocity measurements is that, although $U_e$ decreases with liquid viscosity, the dependence is clearly much weaker than the expected $\sim 1/\eta_l$. The entrainment speed is reduced by a factor 10, while viscosity is varied by a factor 250 (Fig. 3b). Since the liquid inertia is negligible for these highly viscous liquids, this means that the properties of the air must have a significant influence on the entrainment speed. On the other hand, the speed is not determined by the air alone, since that would yield no dependence on $\eta_l$ at all. To reveal the interplay between air and liquid phases, we introduce a dimensionless capillary number, $Ca = U_c \eta_l/\gamma$, that is based on the liquid viscosity. The experimental results are represented in Fig. 4 showing $Ca$ versus the ratio of gas and liquid viscosities $\eta_g/\eta_l$ (closed circles). Clearly, the capillary number for air entrainment displays a dependence that is much stronger than $\sim \ln(\eta_l/\eta_g)$, which is the scaling for air entrainment by liquid jets and the prediction by Ref. [20]. The air thus has a much larger influence than expected. On the same figure we collected data from the coating literature, based on tapes running continuously in a bath, showing a similar trend (various symbols, see caption). Note that in these experiments the contact line typically develops a sharp cusp from which small air bubbles are emitted, rather than an extended air film.

In order to understand the influence of air, one can extend the common lubrication approximation to large slopes and 2 phase flow, but small curvature of the interface. In the spirit of [23, 20], one can start from the analytical solutions of flow in a wedge due to Huh & Scriven, as detailed in the Supplementary Material.
Numerical solution of the model provides the capillary number for entrainment $Ca_e$ as a function of the local slope $\theta$.

$$E_g \sim \frac{\eta_\ell U^2}{\pi - \theta}, \quad E_l \sim \eta_\ell U^2 (\pi - \theta)^2,$$

which is slightly different from the estimates in [14, 15]. Clearly, the dissipation in the gas can dominate over liquid dissipation for contact angles very close to $\pi$, with a cross-over occurring when $\eta_\ell / \eta_\ell \sim (\pi - \theta)^3$. As shown in Fig. 5 such angles indeed appear naturally when the liquid advances rapidly, while this is not the case when the liquid recedes. This explains the marked asymmetry between wetting and dewetting: the faster advancing speed is due to the reduction of dissipation near $\theta \approx \pi$.

In this Letter we experimentally showed that the entrainment speeds of advancing contact lines do not scale as $\gamma / \eta_\ell$, but has a much weaker variation with liquid viscosity. We explain this by the influence of the air flow when the local angle of the interface is close to $\pi$. Can such a scenario explain the observed increase of entrainment speed when depressurizing the air? A pressure reduction does not affect the gas viscosity, but it does increase the mean free path by a factor $\sim \rho_{\text{atm}} / \rho$. Since the mean free path under ambient conditions is approximately 70 nm, it is pushed well into the micron range when pressure is reduced by a factor 100 [26, 27]. The mean free path then becomes comparable to the film thickness measured experimentally (Fig. 3). Interpreting the mean free path of the gas as an effective slip [27, 31], this indeed yields an increase of $Ca_e$ (dotted line in Fig. 4). This suggests that depressurized air acts as a Knudsen gas when confined close to the contact line.

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