**Dynamics of Dewetting at the Nanoscale**

**A large scale Molecular Dynamics Study**

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## Introduction

Experiment shows that displacement of a liquid across a solid surface involves one or more channels of energy dissipation: in particular, viscous dissipation and wetting-line friction (i.e. dissipation in the immediate vicinity of the wetting line). This has lead to several different theoretical models. Over the last 10 years or so, wetting dynamics has also been studied using molecular dynamics (MD) simulations, yielding results that provide a better understanding of the microscopic mechanisms controlling the dynamics of wetting.

Like wetting, the dewetting of solids by liquid films is important in many high-value processes. Experimental studies of dewetting of thin films of simple liquids have shown that the liquid retracts at a constant speed forming a rim at the receding front. Analysis of energy dissipation at the leading and trailing edges of the rim predicts this linear behaviour. Pioneering MD simulation studies and, in particular, those of Koplik and Banavar have revealed film instability leading to spinodal dewetting, the growth of dry spots and the formation of the growing rim, with a constant dewetting velocity and a constant receding contact angle, smaller than the static value.

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During this talk, we will reconsider large-scale MD simulations devoted to dewetting dynamics. We will in particular examine the influence of solid-liquid interaction and film thickness.
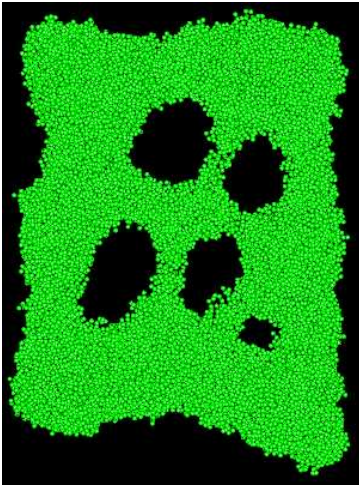
**The results**



*Fig 1: Top view of a thin film of liquid during spontaneous dewetting*

To study the process of dewetting, it is necessary to form a uniform film of liquid on a solid surface with which it does not have a great affinity. If sufficiently thin (typically less than about 1 mm), such a film will spontaneously dewet the solid once a source of instability is created. The construction of the liquid film and initiation of dewetting is conveniently divided into three stages: creating a uniform free film, transferring it to the solid surface, and initiating instability. Once the film is transferred onto the solid surface, we do observe spontaneous dewetting such as illustrated in Fig. 1 where we see nucleation and growth of dry patches along with progressive retraction of the film.

Starting from the initial film, we can remove some band of liquid molecules from the centre of the film to initiate dewetting along two rectilinear fronts. An example of this type of simulation is illustrated in Figure 2 where we present a sequence of snapshots of the system illustrating the progressive retraction of the dewetting fronts and the growth of the rims.
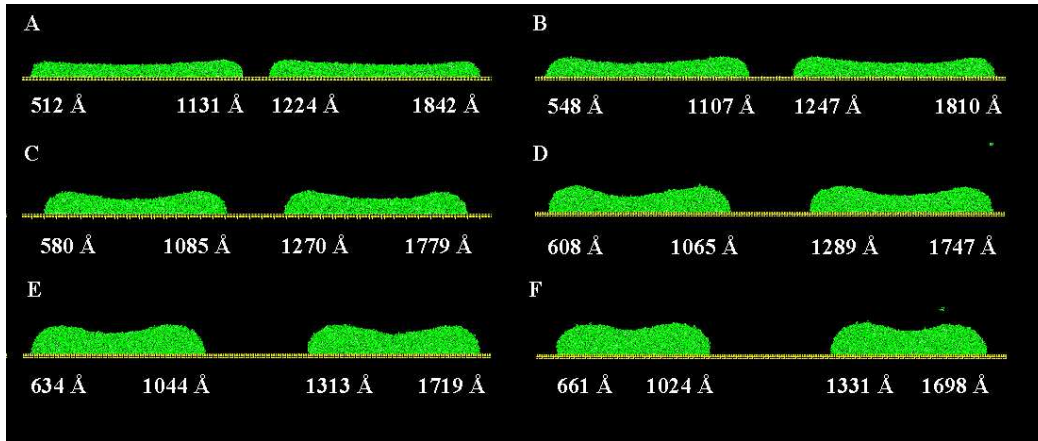
*Fig 2: Sequence of snapshots of the dewetting rim with 297552 liquid atoms and an initial thickness of 30.3 Å*

As we would do in a real experiment, we can locate the edges of the film versus time and extract the partial profile versus time. As an example, Figure 3 shows the superposition of three partial profiles, determined at the start and at two later intervals for the system of Figure 2. Here, we can already discern the growth of a rim of liquid at the dewetting front. A rim is predicted theoretically and has been observed in many experimental studies, as has the constant thickness of the film between the two rims, corresponding to the zone not yet disturbed by dewetting.
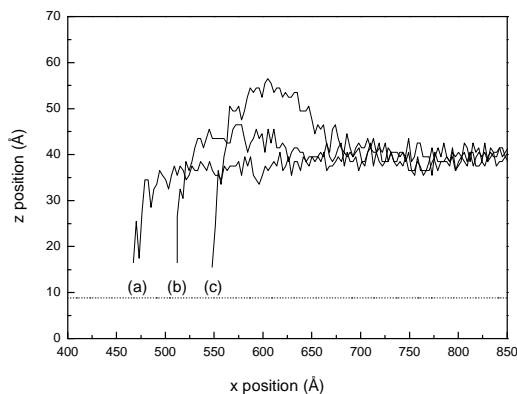


*Fig 3: Superimposed sequence of snapshots of the left edge of the RH half of the film in Fig 2 at (a) iteration O, (b) iteration $10^5$ and (c) iteration $210^5$. The upper surface of the solid is represented by the horizontal dashed line*

This method enables us to study the evolution of the film with time as dewetting proceeds, and so determine important quantities such as the central thickness of the film, the rate of recession of the dewetting fronts, and the contact angle…

Since we can record the positions of the molecules versus time, we also have access to the flow inside the film. As illustrated in Fig. 4, we observe that the molecules move towards the rim upper part and there is a clear evidence of slip in contact with the solid surface.
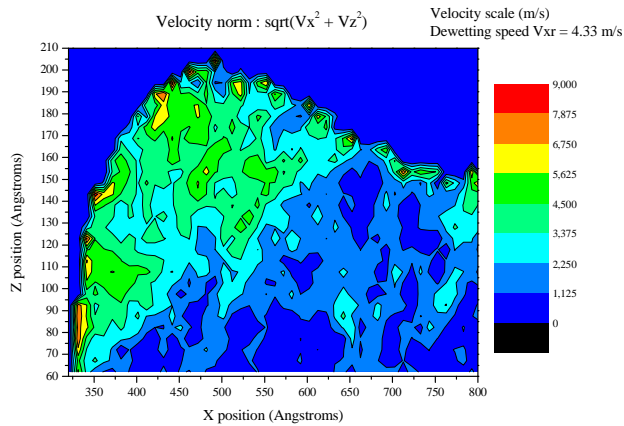


*Fig 4: Typical flow of molecules inside a dewetting rim for a time interval of 25000 iterations.*

It will be shown during the talk that film recession is faster on the more poorly wetted surface to an extent that cannot be explained solely by the increase in the surface tension driving force. Furthermore, the rates of recession of the thinnest films are found to increase with decreasing film thickness such as illustrated in Fig. 5.
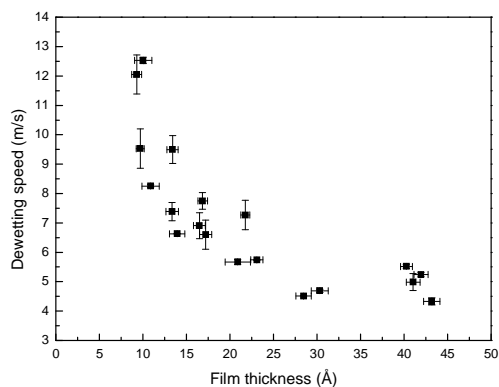


*Fig 5: Typical dewetting speeds as a function of film thickness for a given coupling solid-liquid interaction*

These results suggest not only that the mobility of the liquid molecules adjacent to the solid increases with decreasing solid-liquid interactions, but also that the mobility adjacent to the free surface of the film is higher than in the bulk, so that the average viscosity of the film is a function of thickness. Links with slip-length theories will also be presented.