Boundary Lubrication: Squeeze-out Dynamics of a Compressible 2D Liquid

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The expulsion dynamics of the last liquid monolayer of molecules confined between two surfaces has been analyzed by solving the two-dimensional (2D) Navier-Stokes equation for a compressible liquid. We find that the squeeze-out is characterized by the parameter $g_0 \approx P_0/\rho c^2$, where $P_0$ is the average perpendicular (squeezing) pressure, $\rho$ the liquid (3D) density and $c$ the longitudinal sound velocity in the monolayer film. When $g_0 \ll 1$ the result of the earlier incompressible treatment is recovered. Numerical results for the squeeze-out time, and for the time-dependence of the radius of the squeezed-out region, indicate that compressibility effects may be non-negligible both in time and in space. In space, they dominate at the edge of the squeeze-out region. In time, they are strongest right at the onset of the squeeze-out process, and just before its completion.

I. INTRODUCTION

Sliding friction is one of the oldest problems in physics, and has undoubtedly a huge practical importance.1–11 In recent years, the ability to produce durable low-friction surfaces and lubricants has become an important factor in the miniaturization of moving components in technologically advanced devices. For such applications, the interest is focused on the stability under pressure of thin lubricant films, since the complete squeeze-out of the lubricant from an interface may give rise to cold-welded junctions, resulting in high friction and catastrophically large wear.

It has been shown both experimentally and theoretically that when simple fluids (quasi-spherical molecules and linear hydrocarbons) are confined between atomically flat surfaces at microscopic separations, the behavior of the lubricant is mainly determined by its interaction with the solids that induce layering in the perpendicular direction.4,5,6,7,8,9,10,11. The thinning of the lubrication film under applied pressure occurs step-wise, by expulsion of individual layers. These layering transitions appear to be thermally activated12.13.14.16. Under strong confinement conditions, some lubricant fluids become solid-like.4,5,6,7,8,9,10,11. Other fluids, notably water17,18, remain liquid-like up to the last layer that can be removed upon squeezing. This is related to the expansion of water upon freezing19,20, and should also hold for other liquids which expand upon freezing.

The phenomenology of layering transitions in 2D-solid-like boundary lubrication has been studied in Ref.20.21.22. It has been shown in a series of computer simulations that for solid-like layers, the layering transitions are sometimes initiated by a disordering transition, after which the lubricant behaves in a liquid-like manner for the rest of the squeeze-out process. Since the typical lateral extension in surface force apparatus (SFA) experiments is of order 10-100 μm (much greater than atomic dimensions), it is reasonable to expect that during the layering transition the squeeze-out can be described in the framework of 2D continuum fluid mechanics.

For the first time such squeeze-out layering transitions were quite recently observed in a chain alcohol, C11H23OH (Ref.23,24), by imaging the lateral variation of the gap between the two anvil surfaces as a function of time. These experiments addressed the $n = 1 \rightarrow 0$ transition. More recently, in a refined experimental setup, Mugele et al.25 were able to image several layering transitions ($n \rightarrow n - 1$, $n = 5, 4, 3$) of the silicon oil OMCTS (spherical molecule, diameter ~ 10 Å) in great detail.

FIG. 1: Because of the curvature of the solid walls at the boundary line, the perpendicular pressure $P_0$ will give rise to a parallel force component acting on the 2D-lubrication film. (Schematic.)

The basic theory of 2D squeeze-out dynamics was outlined in Ref.12. Initially the system is trapped in a meta-stable state at the initial film thickness. Squeeze-out starts by a thermally activated nucleation process in which a density fluctuation forms a small hole, of critical radius $R_c \sim 10$ Å. Once formed, a 2D pressure difference $\Delta P$ develops between the boundary line separating the squeezed out region from the rest of the system, and
the outer (roughly circular) boundary line of the contact area, thus driving out the rest of the 2D fluid. The origin of $\Delta p$ is the elastic relaxation of the confining solids at the boundary line as is illustrated in Fig. 1.

All earlier analytical studies of squeeze out have assumed that the lubricant behaves as an incompressible 2D liquid. While that assumption is quite good for many practical situations, recent computer simulations have shown that, at least at high squeezing pressures, strong density fluctuations may occur in the lubrication film. For example, in Ref. 26 it was found that during the layering transition $n = 2 \rightarrow 1$, while islands of (temporarily) trapped bilayer ($n = 2$) were removed by being squeezed into the monolayer, the density of the monolayer film was much higher in the region close to the trapped $n = 2$ islands than further away. This resulted in a 2D pressure gradient in the film which induced a flow of the lubricant molecules away from the trapped islands. This kind of situations clearly calls for a consideration of the finite compressibility of the film.

In this paper we study the dynamics of the expulsion of the last liquid monolayer of molecules confined between two surfaces by solving the two-dimensional (2D) Navier-Stokes equation for a compressible liquid monolayer. We find that the squeeze-out is characterized by the parameter $g_0 \approx P_0/\rho c^2$, where $P_0$ is the average perpendicular (squeezing) pressure, $\rho$ the liquid (3D) density and $c$ the longitudinal sound velocity in the monolayer film. When $g_0 \ll 1$ the 2D liquid can be considered as incompressible, in which case the results of the earlier treatment are reproduced. We present numerical results for the squeeze-out time, and for the time-dependence of the radius of the squeezed-out region, for several values of the parameter $g_0$. The main changes due to compressibility occur right at the onset of the squeeze-out process, and just before its completion.

II. THEORY

We assume the lubricant film to be in a 2D-liquid-like state, and the squeeze-out to be described by the 2D Navier-Stokes equations. For a compressible 2D liquid these equations take the form

$$\frac{\partial n}{\partial t} + \nabla \cdot (nv) = 0 \tag{1}$$

$$\frac{\partial v}{\partial t} + v \cdot \nabla v = -\frac{1}{mn} \nabla p$$

$$+ \nu_1 \nabla^2 v + \nu_2 \nabla \nabla \cdot v - \bar{\eta} v \tag{2}$$

where $mn$ and $v$ are the local 2D mass density and the velocity of the fluid, $p$ is the 2D-pressure, $\nu_1$ and $\nu_2$ are viscosities. The last term in (2), i.e. $-\bar{\eta} v$, describes the drag force acting on the fluid as it slides relatively to the solid walls. The magnitude of the friction also depends on the nature of the solid walls, e.g. on the amplitude of the atomic corrugation and on the structure of the solid walls (amorphous vs. crystalline, commensurate vs. incommensurate). As long as the lubricant can be considered as a 2D fluid, as in the recent squeeze out experiments by Mugele et al., all the details of the solid walls are properly taken into account by the friction coefficient $\bar{\eta}$. In principle $\bar{\eta}$ depends on the normal pressure too, but in the measurements of Mugele et al. this dependence is slight enough that it appears to be negligible.

Simple dimensional arguments (see Ref. 26) show that one can usually neglect the nonlinear and the viscosity terms in (2), and that one can also assume the velocity field to change so slowly that the time derivative term can be neglected too. Thus,

$$\nabla p + mn\bar{\eta}v = 0. \tag{3}$$

In what follows we will assume that the squeeze-out nucleated in the center ($r = 0$) of the contact area, and spread circularly towards the periphery. The 2D-pressure $p$ at the outer boundary $r = R$ of the contact area takes the constant value $p_0$ (the spreading pressure) while it takes a higher value $p_1$ at the inner boundary towards the $n = 0$ area (Fig. 1). In fact, if $P(r)$ is the perpendicular pressure acting in the contact area, then $p_1(r) = p_0 + P(r) a$, where $a$ is the thickness of the monolayer (see Ref. 26). We may in most practical applications assume a Hertz contact pressure

$$P(r) = \frac{3}{2} P_0 \left(1 - \frac{r^2}{R^2}\right)^{1/2} \tag{4}$$

Finally, in order to have a complete set of equations we must specify the relation between the 2D pressure $p$ and the 2D density $n$. We will assume that

$$p = p_0 + mc^2(n - n_0) \tag{5}$$

where the compressibility is $B = 1/mc^2$, $c$ being the longitudinal 2D sound velocity. Here $n_0$ is the 2D lubricant density at the periphery $r = R$ of the contact area.

Writing the velocity field as $v = \hat{v} v(t)$, equations (1) and (3) takes the form

$$\frac{\partial n}{\partial t} + \left(\frac{\partial}{\partial r} + \frac{1}{r}\right) (nv) = 0 \tag{6}$$

$$\frac{\partial p}{\partial r} + mn\bar{\eta}v = 0$$

Using (5) the last equation takes the form

$$\frac{\partial n}{\partial r} + \frac{\bar{\eta}}{c^2} (nv) = 0 \tag{7}$$

Combining (6) and (7) gives

$$\frac{\partial n}{\partial t} - \frac{c^2}{\bar{\eta}} \left(\frac{\partial}{\partial r} + \frac{1}{r}\right) \frac{\partial n}{\partial r} = 0 \tag{8}$$
The density $n$ satisfies the boundary conditions

$$n(R, t) = n_0$$

where $R = r(t)$ is the equation for the inner boundary line. Finally, we note that the velocity $v(r_1(t), t)$ of the 2D-liquid at the inner boundary $r = r_1(t)$ must equal the radial velocity $r_1(t)$ of the boundary line. Thus, if we put $r = r_1(t)$ and $v(r_1(t), t) = \dot{r}_1(t)$ in (7) we get

$$\frac{\partial n}{\partial t}(r_1(t), t) = -\frac{\bar{\eta}}{c^2}n(r_1(t), t)\dot{r}_1$$

Let us at this point introduce dimensionless variables. If we measure the radius $r$ in units of $R$, time $t$ in units of $\tau = \bar{\eta}R^2/c^2$ and density $n$ in units of $n_0$ we get

$$\frac{\partial n}{\partial t} = \frac{\partial}{\partial r} \left( \frac{\partial}{\partial r} + \frac{1}{r} \right) \frac{\partial n}{\partial r} = 0$$

and the boundary conditions becomes

$$n(1, t) = 1$$

$$n(r_1(t), t) = 1 + g(t)$$

and

$$\frac{\partial n}{\partial r}(r_1(t), t) = -[1 + g(t)]\dot{r}_1$$

where

$$g(t) = amc^2n_0$$

If we assume that $P(r)$ is of the Hertz form, then

$$g(t) = g_0 \frac{3}{2} (1 - [r_1(t)]^2)^{1/2}$$

where

$$g_0 = \frac{aP_0}{mc^2n_0}$$

Thus, the theory depends only on a single parameter $g_0$. Note that $n_0/a \approx \rho$, where $\rho$ is the 3D density of the liquid, and with the typical values $\rho \approx 1000$ kg/m$^3$ and $c \approx 700$ m/s we get $\rho c^2 \approx 500$ MPa. In the experimental studies by Mugele and Salmeron (as well as in most other Surface Force Apparatus studies) the average squeezing pressure $P_0 \ll 500$ MPa which implies that the liquid can be considered as incompressible and the theory developed elsewhere can be used. However, in many practical situations the pressure $P_0$ might be similar to the yield stress of the solids which for metals is typically of order $\sim 1000$ MPa. In these cases it is necessary to include the finite compressibility of the lubricant in order to accurately describe the squeeze-out dynamics. In Sec. III we shall present numerical results based on the above equations for a range of values of the parameter $g_0$.

Let us first calculate the squeeze-out time in the limit when the compressibility $B = \infty$. In this limit, all the adsorbates from the region $r < r_1(t)$ will be piled-up right at the boundary line $r = r_1$. If we consider a small angular section $\Delta \phi$ then the driving force acting on the boundary line is $F = r_1\Delta \phi [p_1 - p_0] = r_1\Delta \phi P(r_1)a$. This must balance the frictional drag force which is $Nm\bar{\eta}$ where the number of adsorbates $N = \pi r_1^2(\Delta \phi/2\pi)n_0$. Thus we get

$$\dot{r}_1 = \frac{2P(r)a}{n_0m\bar{\eta}}$$

Assume first that $P = P_0$ is constant. Thus, (19) gives

$$\dot{r}_1 r_1 = \frac{R^2}{2T}$$

where

$$T = \frac{mn_0\bar{\eta}R^2}{4P_0a}$$

is the squeeze-out time for an incompressible 2D fluid, see Ref. Integrating (20) gives

$$\frac{r_1(t)}{R} = \left( \frac{t}{T} \right)^{1/2}$$

so that the squeeze-out time, $T^*$, in the limit $B = \infty$ is the same as for an incompressible 2D-fluid, $T^* = T$. This suggests that the squeeze-out time is independent of the compressibility of the 2D-liquid, which our numerical simulations presented below indeed show to be the case.

Next, let us assume that the perpendicular pressure is of the Hertz form, appropriate for a fluid between curved surfaces. In that case (19) gives

$$\dot{r}_1 = \frac{R^2}{2T} \left[ 1 - \left( \frac{r_1}{R} \right)^2 \right]^{1/2}$$

or, with $r_1^2/R^2 = \xi$,

$$\int_0^{r_1^2/R^2} \frac{d\xi}{(1 - \xi)^{1/2}} = \frac{3t}{2T}$$

Performing the integral gives

$$\left[ 1 - \left( \frac{r_1}{R} \right)^2 \right]^{1/2} = 1 - \frac{3t}{4T}$$

Thus, the squeeze-out time for the Hertzian contact pressure is $T_{H}^* = 4T/3$, and the time dependence of $r_1(t)$ is given by

$$\frac{r_1}{R} = \left[ \frac{3t}{2T} \right]^{1/2} \left( 1 - \frac{3t}{8T} \right)^{1/2}$$
or

\[
r_1 = \left(\frac{2t}{T_H}\right)^{1/2} \left(1 - \frac{t}{2T_H}\right)^{1/2}
\]

The squeeze-out time for an incompressible fluid with a Hertzian contact pressure is \(T_H = (4T/3)(2 - \ln4) \approx 0.8183\ T\), which is a factor \(2 - \ln4 \approx 0.6137\) smaller than for the \(B = \infty\) limiting case. Thus, for a Hertzian contact pressure the squeeze-out time does depend on the compressibility of the 2D lubrication film.

### III. NUMERICAL RESULTS

We consider first the case of a spatially constant squeezing pressure, \(P(r) = P_0\), appropriate for a fluid between flat surfaces. In this case numerical calculations show that the squeeze-out time is independent of the compressibility, i.e., independent of the parameter \(g_0\). However, the time dependence of the squeeze-out radius \(r_1(t)\) does depend on \(g_0\). In Fig. 2(a) we show this time dependence for four cases, \(g_0 = 0, 0.2, 0.5\), and 2. In Fig. 2(b) we show the adsorbate density profile at the time point when the squeeze-out radius \(r_1 = 0.3R\), for the same four \(g_0\)-values as in (a).

Let us now assume the Hertzian squeezing pressure profile, \(P(r) = P_H(r)\). In this case the squeeze-out time depends on the compressibility, increasing from \(T_H \approx 0.8183\ T\) to \(1.3333\ T\) as the compressibility increases from \(B = 0\) to \(\infty\). In Fig. 3(a) we show the squeeze-out time as a function of \(g_0\). In Fig. 3(b) we show the time dependence of \(r_1(t)\) for four cases, \(g_0 = 0, 0.2, 0.5\), and 2. In Fig. 3(b) we show the adsorbate density profile at the time point when the squeeze-out radius \(r_1 = 0.3R\), for the same four \(g_0\)-values as in (a). The results of Fig. 2 and Fig. 3 show that a compressibility parameter \(g_0\) as small as 0.2 should produce a measurable difference in the squeeze-out evolution at all times. The main effect of compressibility appears at the beginning and at the end of the squeeze-out process. Initially, compressibility favors piling up of fluid at the squeeze-out boundary, which can as a result expand more rapidly, compared with the case of an incompressible fluid. On the other hand, when the fluid approaches the boundary of the contact region, the squeezing-out speed of the compressed fluid is smaller, due to its increased density and, consequently, friction. In the case of uniform squeezing pressure these two effects compensate exactly, leading to a total squeeze-out time independent of the compressibility. For a Hertzian pressure distribution, the squeeze-out time instead increases with increasing compressibility: the initial speed up is overcompensated by the enhanced friction at the periphery of the contact area.

![Figure 2](image2.png)

**FIG. 2:** Constant squeezing pressure, \(P(r) = P_0\). (a) Squeeze-out radius \(r_1\) (in units of the radius \(R\) of the contact area) versus time (in units of the squeeze-out time). We show results for four different cases, namely \(g_0 = 0\) (corresponding to an incompressible adsorbate layer), 0.2, 0.5, and 2. (b) Adsorbate density distribution \(n(r)\) (in units of the natural density \(n_0\)) during squeeze-out, for the same four cases as in (a) at a time when the squeeze-out radius \(r_1 = 0.3R\).

![Figure 3](image3.png)

**FIG. 3:** Dependence of the squeeze-out time on the compressibility parameter \(g_0\) for a Hertzian squeezing pressure.
IV. SUMMARY

The continuum mechanics theory of squeeze-out has been solved numerically for a 2D compressible liquid. We considered both a constant normal stress, and a Hertzian normal stress, and assumed a centro-symmetric squeeze-out. We found that the squeeze-out is completely characterized by the compressibility parameter \( g_0 \approx P_0/\rho c^2 \), where \( P_0 \) is the average perpendicular squeezing pressure, \( \rho \) the (3D) liquid density and \( c \) the longitudinal sound velocity in the monolayer film. When \( g_0 \ll 1 \) the 2D liquid can be considered incompressible, and the earlier results are reproduced. We presented numerical results for the squeeze-out time, and for the time dependence of the squeeze-out radius, for a grid of values of the parameter \( g_0 \). For a constant squeezing pressure, the squeeze-out time was found to be independent of the compressibility parameter \( g_0 \), while for a Hertzian contact pressure it increased slightly with increasing \( g_0 \). It is hoped that these theoretical results will soon be submitted to experimental check.

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