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Rolling droplets

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A droplet of nonwetting viscous liquid moves on an inclined plane by rolling along it. We give a scaling law for the uniform speed of such a droplet. We then analyze the flow in the contact region and show that the classical stress singularity at the contact line is alleviated in this case. © *1999 American Institute of Physics.* [S1070-6631(99)01609-8]

I. INTRODUCTION

When a rigid circular cylinder or sphere is placed on a rough inclined plane it will roll down the plane. When the experiment is repeated with a rigid cube it will slide down the plane. If the object is deformable a variety of motions become possible; the motion of elastic bodies and fluid drops depends on the interfacial energies of the materials, the roughness of the interfaces, the size of the objects, etc. This is because a deformable body maintains contact with the surface over a finite area. For a viscous fluid droplet, two possible motions may ensue. If the droplet partially wets the surface it slides along it, while if the droplet is nonwetting, it can roll on the surface, much like an elastic body when viewed from the exterior. Here we consider the motion of a small nonwetting droplet forced by a weak gravitational field. A classic example of this motion is exhibited by a droplet of mercury on an inclined plane and is probably the origin of the name quicksilver, after the Latin *Argentum Vivum* for the swiftly moving droplet of the silvery liquid.

For such motions to be observable, we must have liquids with high surface tension moving on very clean hydrophobic surfaces. Until recently, only chemically treated surfaces were amenable to such experiments that allowed for large contact angles; however, these surfaces were easily contaminated. Recently it has become possible to vary the surface roughness[9] to achieve contact angles very close to 180° thus making robust experiments in the high contact angle regime more accessible. A small droplet rolling down such an incline then would reach a steady velocity determined by the balance between the rate of energy dissipation due to internal viscous motions and the rate of change of gravitational potential energy.

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II. VELOCITY OF A ROLLING DROPLET

We consider a small nonwetting droplet of fluid with viscosity μ, surface tension σ, density ρ, nominal radius R moving down a plane inclined at an angle $\alpha \ll 1$ with the horizontal. For a small enough droplet, surface tension forces will dominate gravitational forces; in dimensionless terms the Bond number $\mathrm{Bo} = \rho g R^2/\sigma \ll 1$. We also assume that viscous effects dominate inertia so that a nominal Reynolds number $\mathrm{Re} = \rho L V/\mu \ll 1$, where V is a characteristic velocity and L is a characteristic length which we will determine later. Finally, we assume that the droplet is moving at small enough velocities, so that its shape does not change a lot due to the flow so that the Capillary number $\mathrm{Ca} = \mu V/\sigma \ll 1$. The relative magnitude of these dimensionless parameters will become clearer as we proceed.

When the droplet is at rest on a horizontal substrate, its shape and the area of contact with the solid are determined by the balance between capillary and gravity forces. For $\mathrm{Bo} \ll 1$, the droplet is almost spherical everywhere except in the neighborhood of the substrate, where it is a flat horizontal disk. The lowering of the center of the droplet by δ due to its own weight and the radius of the contact disc l are related to each other by

$$l^2 \sim R\delta, \tag{1}$$

where $\sim$ means ''of the order of.'' Equation (1) corresponds to an approximation to the shape of the droplet in the vicinity of the substrate, valid for weakly deformed droplets or solids.[7] There is an increase in the surface area Δa associated with this shape change due to two contributions both of which are of the same order. The first is due to the reduction in the area of the spherical cap when flattened into a disc, and is given by $\Delta a_1 \sim l^2(1-\cos\theta)$ where 2θ is the angle subtended by the disc at the center of the droplet. Since $\theta \sim l/2R$, this yields $\Delta a_1 \sim l^4/R^2$. The second is an increase in the area due to the the transfer of the volume of the spherical cap to the rest of the droplet. The volume of the cap is $l^2\delta$

$\sim l^4/R$. If ΔR is the change in the radius of the sphere due to this additional volume, then $R^2\Delta R \sim l^4/R$ so that $\Delta R \sim l^4/R^3$, and the corresponding area change $\Delta a_2 \sim R\Delta R \sim l^4/R^2$. Since a sphere has the least area for a given volume, the sum of the two contributions $\Delta a_1 + \Delta a_2$ is positive. The increase in surface energy $\sigma(\Delta a_1 + \Delta a_2)$ is achieved at the cost of lowering the potential energy of the droplet $\rho g R^3 \delta$, so that

$$\rho g R^3 \delta \sim \frac{\sigma l^4}{R^2}. \tag{2}$$

Here we have assumed that the surface energy per unit area for the liquid–solid surface is of the same order as the liquid–gas interface, corresponding to having a thin layer of vapor between the liquid and solid. Solving Eqs. (1) and (2) for δ and l yields

$$\delta \sim \frac{\rho g R^3}{\sigma} = \mathrm{Bo}R, \quad l \sim \left(\frac{\rho g}{\sigma}\right)^{1/2} R^2 = \mathrm{Bo}^{1/2} R. \tag{3}$$

Substituting in typical values for ρ,σ for mercury and water, we find that for capillary forces to dominate gravity, the size of the drop must be of the order of 10^{-3} m, as must the radius of the contact disk l. By changing the liquid we can lower its density by an order of magnitude, while gravity can be reduced by going into a microgravity environment, so that the size of a sessile droplet can be increased by as much as an order of magnitude, while still keeping it.

This classical scaling corresponds to the case of a static droplet with capillary number $\mathrm{Ca} = \mu U/\sigma = 0$. When the droplet moves on a weakly inclined plane, the change in shape and thereby in the above scaling is negligible. In steady rolling motion along the plane, the velocity of the droplet is determined by the balance between viscous dissipation and the rate of decrease of the gravitational potential energy, i.e.

$$UR^3 \rho g \sin\alpha \sim \mu \int_{V_d} (\nabla \mathbf{u})^2 dV. \tag{4}$$

Here V_d is the volume over which viscous dissipation occurs, U is the velocity of the center of mass of the droplet, and $\mathbf{u}$ is the velocity field in the droplet. To estimate the viscous dissipation, we recall that for Stokes flow, given a set of boundary conditions, the flow is such that the viscous dissipation is a minimum.[13] This is achieved by maximizing the volume over which the droplet is in rigid rotation, since this induces no dissipation. If the contact between the droplet and the substrate were restricted to a point, this would be achieved by a Huygens motion, i.e., instantaneous rigid rotation about a horizontal axis passing through this point, which satisfies the condition of no-slip and makes the rate of dissipation vanish. Of course, for finite Bo, contact occurs over a disc of size l. Then the dissipation is restricted to a neighborhood of this disc, where the velocity field is not a simple rigid rotation. However, far from the contact region the droplet moves in a manner similar to rigid rotation about an axis passing through the area of contact.

Due to the elliptic nature of the problem the influence of the contact area extends into the droplet to a height l, similar to the Hertz contact problem in elasticity.[7] The magnitude of the fluid velocity in this region is $|\mathbf{u}| \sim lU/R$ so that $|\nabla \mathbf{u}| \sim U/R$. Viscous dissipation occurs in a volume determined by the extent of the influence of the contact region so that $V_d \sim l^3$. Substituting these results into Eq. (4) and solving for the steady-state velocity yields

$$U \sim \frac{R^5 \rho g \sin\alpha}{\mu l^3} = \frac{\sigma^{3/2} \sin\alpha}{\mu R (\rho g)^{1/2}} \sim \frac{\sigma \mathrm{Bo}^{-1/2} \sin\alpha}{\mu}. \tag{5}$$

This counter-intuitive relation of the velocity to the drop size may be explained thus: Although the driving force increases with the size of the droplet (as R^3), the viscous forces increase faster (as R^4) because of the rapid increase of the contact disk radius with droplet size. To quantify the regime of validity of these results which describe the rolling of small nonwetting viscous droplets on a slightly inclined plane, we recall that the typical fluid velocity in the vicinity of the contact disk is $V \sim Ul/R$, so that a typical capillary number $\mathrm{Ca}_* \sim \mu V/\sigma \sim \sin\alpha$, which is much less than unity, as assumed earlier. Furthermore a typical Reynolds number $\mathrm{Re}_* \sim \rho V l/\mu = \rho^{3/2}(\sigma g)^{1/2} R^2 \sin\alpha/\mu^2 \ll 1$ for this analysis to be valid. In dimensionless terms this reads $R^2 \ll R_m^2/\sin\alpha$, where $R_m = \mu/(\rho^3 \sigma g)^{1/4}$ and thus leads to a maximum droplet size. Substituting in the appropriate parameters for mercury or water on an inclined plane of angle 10°, we find that $R_m \sim 0.001$ mm! On the other hand, by making the angle of the inclined plane very small or by using a very viscous liquid, R_m can be made macroscopic, so that a rolling droplet of liquid that is thousand times more viscous than water can be as large as 1 mm, move at a few cm/s and still constitute a low Re flow.

We now estimate the viscous dissipation in the bulk of the droplet away from the region that is influenced by the contact region. Here there will be small deviations from the purely rotational velocity field given by lU/R. Velocity perturbations u' from this Huygens motion vary inversely as the scaled distance from the contact area, in a manner similar to the velocity field generated by a sphere creeping through a viscous fluid, so that $u' \sim l^2 U/R^2$. Then the dissipation in the bulk given by $\mu \int_V (\nabla u')^2 dV \sim \mu U^2 l^4/R^3$ is dominated by the dissipation $\mu U^2 l^3/R^2$ in the contact region, as long as $l/R \ll 1$, i.e., $\mathrm{Bo} \ll 1$, as is the case here.

When the drop size is much larger than the capillary length $(\sigma/\rho g)^{1/2}$, the surface of contact is no longer parabolic. In this case, the drop resembles a pancake of thickness w and contact disk size L. To determine these quantities, we consider the following functional:

$$F \sim \sigma(L^2 + Lw) - \rho g R^3 w + \lambda(L^2 w - R^3), \tag{6}$$

where the first term corresponds to the surface energy, the second to the gravitational energy and the third enforces the constant volume constraint, with λ being the pressure. Assuming that $w \ll L$, and extremizing the functional with respect to L, w, λ yields

$$\lambda = \sigma/w, \quad L \sim \left(\frac{\rho g}{\sigma}\right)^{1/4} R^{3/4}, \quad w \sim \left(\frac{\sigma}{\rho g}\right)^{1/2}. \tag{7}$$

We observe in particular that the thickness of the pancake $w \ll L$ is independent of the size of the drop, and is in fact just the capillary length. When this pancake rolls down an inclined plane, the velocity gradient scales as U/w, so that balancing the viscous dissipation rate with the rate of gravitational energy gain yields $\mu(U/w)^2 R^3 \sim \rho R^3 U g \sin\alpha$. Substituting in for w from Eq. (7) leads to the following scaling relation for the velocity of large pancake drops:

$$U \sim \left(\frac{\sigma g}{\nu^2}\right)^{1/2} \sin\alpha. \tag{8}$$

Recent experiments motivated by our theory[12] are consistent with the above scenario. On low-angle inclined planes made of nearly nonwetting substrates, smaller drops of a viscous liquid in the Stokesian regime do indeed travel faster than large ones, and confirm that the velocity varies inversely with the size of the drop [Eq. (5)], with the velocity eventually reaching a constant value as the drop size becomes vary large [Eq. (8)]. The experiments were done with droplets of glycerol of viscosity 10 gm/cm.s and a typical size of 1 mm, giving rise to observed velocities in the range of a few cm/s, as predicted by the scaling law [Eq. (5)].

III. CONTACT LINE DYNAMICS

Next, we consider the velocity field inside the droplet, in particular near the advancing contact line. We focus on the two-dimensional case here for simplicity of exposition. The order of magnitude estimates are not very different in the three-dimensional case because the essential property of the velocity field, that it is tangential to the surface at the contact line, is common to both cases. Following our earlier discussion, the velocity field far from the contact region is close to a pure rotation about a horizontal axis passing through the contact region. However, this assumption is invalid near the contact region; here we must solve Stokes equations for the free surface of the droplet subject to the usual boundary conditions on the contact line and the fluid–air free surface. This latter problem of the dynamics of a triple point, i.e., the solid–liquid–vapor interface, has been the subject of enormous study and controversy.[3] The starting point of most studies on this problem goes back to Ref. 6 who highlighted the stress singularity at the contact line associated with a similarity solution to Stokes flow in a wedge of fixed geometry. Recently, this subject has been visited from the perspective of diffuse-interface models to account for mass transfer by evaporation–condensation,[14] and leads to a problem in matched asymptotic expansions with different force balances in regions close to and far from the contact line wedge. This wedge is defined for all values of contact angle except 180°, which corresponds to a rolling droplet considered here. In this special case, the interface merges smoothly with the immovable substrate and its shape must be determined as part of the solution of the boundary-value problem. Prior studies of this mathematical problem in Refs. 2 and 10, are marred by an error in the boundary condition pointed out in Ref. 8.

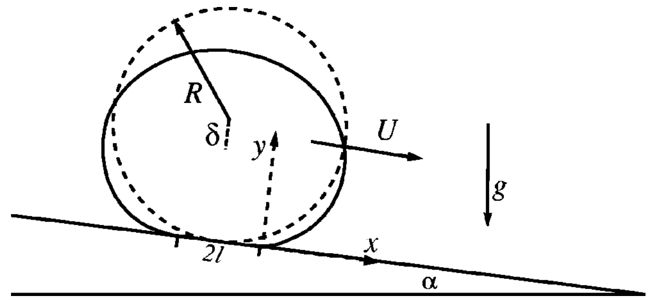

FIG. 1. Schematic of a nonwetting droplet of radius R, on an inclined plane of angle $\alpha \ll 1$. The contact disc is of diameter $2l$ and the center of mass is displaced by an amount δ due to the weight of the droplet. The coordinate system is centered at the advancing contact line which is tangential to the inclined plane.

Unfortunately, all these papers also neglect a crucial hydrostatic pressure term without which we cannot analyze the dynamics of the slow rolling of a small droplet that we are interested in here.

As the dense fluid rolls down the inclined plane, it squeezes out the light fluid (air) in the neighborhood of the contact line. We neglect the effects of air as the viscous stress in it is scaled by the density of the fluid. The Stokes equations in the denser fluid can be rewritten in terms of a stream function $\psi(x,y)$ which satisfies the biharmonic equation

$$\nabla^4 \psi = 0. \tag{9}$$

The coordinate system is as shown in Fig. 1, with the advancing contact line which has a vanishing contact angle located at the origin and the inclined plane coinciding with $y=0$. The velocity field $\mathbf{u}=(u,v)$ in this coordinate system is given by $u=\partial\psi/\partial y$, $v=-\partial\psi/\partial x$. The boundary condition of no-slip along the inclined plane corresponds to

$$\frac{\partial\psi}{\partial y} = \frac{\partial\psi}{\partial x} = O, \quad y=0, \quad x<0. \tag{10}$$

On the free surface of the droplet, three conditions must be satisfied: The free surface must be a material surface, the tangential stress must vanish and the normal stress must be balanced by the surface tension. For small droplet velocities, the viscous stress is dominated by capillary forces, i.e., Ca $=\mu U/\sigma \ll 1$, even near the contact line. Then the free surface does not deviate too much from its static equilibrium shape and the leading order balance of normal stresses yields the Young–Laplace equation, whose solution gives the shape of the free surface

$$y = \frac{x^2}{2R}, \quad x>0. \tag{11}$$

Here we differ from Refs. 2, 8, and 10 who assume that the dominant terms in the balance of normal stresses near the contact line arise from viscous forces and capillarity. This leads to an equation for the unknown free-surface of the form $y=ax^q$, $q>2$, $x>0$. The viscous-capillary balance in Refs. 2, 8, and 10 is a consequence of dropping the term corresponding to the hydrostatic pressure, and is incorrect in the case of a finite droplet with a nonvanishing internal pressure. In the absence of motion (and viscous stresses) the hydrostatic pressure p inside the droplet is balanced by the capillary pressure, and is a smooth nonconstant function of location inside the drop. Thus the radius of curvature on the free surface is finite and fixed everywhere and in particular at the contact line, and is given by the Young–Laplace law. If the radius of curvature remains finite along the contact line during motion, the correction to the normal stress balance equation due to viscous forces is relatively small everywhere and in particular at the contact line. This requires $q=2$ and yields a consistent smooth solution for a moving contact line on a dry surface.

The kinematic condition at the free surface requires that the normal component of the fluid velocity equals the velocity of the droplet. If $\mathbf{n}=(-x/R,1)$ is the unit normal to the free surface and $\mathbf{U}$ is the droplet velocity, then

$$\mathbf{n}.(U-.\mathbf{u})=0, \quad y=\frac{x^2}{2R}. \tag{12}$$

Finally the condition of no tangential stress on the free surface of the droplet reads

$$\mathbf{n}.\nabla(\mathbf{u}-(\mathbf{n}.\mathbf{u})\mathbf{n})=0, \quad y=\frac{x^2}{2R}. \tag{13}$$

In the neighborhood of the leading contact line $x=y=0$, we use polar coordinates r,θ and look for a stream function of the form $\psi=r^n\phi(\theta)$. For $\theta \ll 1$, $r\sim x$, $\theta \sim y/R$. Then, $r=0$ corresponds to the leading contact line, and $\theta=\pi(0)$ is the wet(dry) half-line along the inclined plane. To leading order, the conditions (10), (12)–(13) are then rewritten as

$$\begin{aligned}
&\phi(\theta)=\frac{d\phi}{d\theta}=0, \quad \theta=\pi,\\
&\frac{d\psi}{dr}=-\frac{rU}{R}, \quad \theta=0, \qquad (14)\\
&\frac{d^2\phi}{d\theta^2}=0, \quad \theta=0.
\end{aligned}$$

The solution to Eq. (9) subject to Eqs. (11) and (14) is

$$\psi=-\frac{r^2U}{2R}\left(1-\frac{\theta}{\pi}+\frac{\sin 2\theta}{2\pi}\right). \tag{15}$$

We observe that the stream function and its derivatives are bounded everywhere in the neighborhood of the contact line, i.e., there is no singularity in either the force or the stress at the contact line. Furthermore, the only roots of $\psi=0$ in the interval $(0,\pi)$ are $\theta=0,\pi$. Thus the only material surfaces merging at the contact line are the free surface and the solid surface (to leading order). If the calculation were carried to O(Ca), there would be a new surface that delineates the region of the droplet where there is recirculation, seen in two-dimensional numerical simulations.[5]

IV. DISCUSSION

We conclude with a discussion of our results and their implications. The simple scaling law (5) for the velocity of droplet of a viscous liquid with a contact angle of 180° rolling down an inclined plane is valid only when the plane has a small slope, the size of the droplet is much smaller than its capillary length, and when the drop is moving slowly. As the drop size is increased still further eventually the contact area does not grow any faster than the size, so that the velocity of large viscous drops becomes size-independent, as long as $\mathrm{Re} \ll 1$. While this Stokesian regime is accesible with very viscous liquids for a rolling droplet of water of size ~1 mm and typical typical velocities of the order of 1 cm/s suggest that inertial effects in the bulk and the surface may become important. That capillary waves are not excited may be deduced from the dispersion relation relating the wave number k to the frequency ω given by $\omega^2 \sim \sigma k^3$. Upon substituting $k \sim R^{-1}$, gives $u \sim (\sigma/R)^{1/2} \sim 8$ cm/s which is much larger than the typical droplet velocity. Inertial effects during rapid rolling are limited to a boundary layer of thickness $\Delta \sim (\nu R/U)^{1/2}$. Then the dissipation is limited to a region of volume $l^2\Delta$ and we get a different estimate for the terminal velocity of a rolling droplet, given as $U \sim R^{-5/3}(g \sin\alpha)^{2/3}(\sigma/\rho g)^{4/3}/\nu^{1/3}$. Equating this estimate for the velocity to the one obtained when viscous contributions dominate [Eq. (5)] yields a droplet size characterizing the crossover from viscous to inertial motion which occurs when $R_* \sim \nu(\rho/g\sigma \sin^2\alpha)^{1/4}$. For water on an inclined plane at an angle of 10°, this yields $R_* \sim 0.1$ mm; however, it is likely that the transition to inertial flow occurs much more quickly as the drop deforms in response to the flow.[1]

Our leading order perturbation theory of the flow field in the neighborhood of the contact line in a rolling droplet reveals a nonsingular stress field correcting earlier attempts to solve this problem. If the contact angle is not 180°, the surface of the droplet does not merge smoothly with the substrate. In the absence of a universally accepted theory for the motion of a moving contact line, we can only speculate on the corrections brought about by a contact angle of say 179°. Presumably, following what we have shown for the 180° case, the viscous forces are still much smaller than than the capillary forces near the contact line. While a coherent asymptotic theory for this problem is beyond the scope of this note, phase field models[11,14] provide a regularized approach to the study of these lubrication flows for small and large contact angles.

The above scaling analysis can be modified to understand rolling motion due to forces other than gravity such as those induced by electrohydrodynamic or chemical effects. Interesting examples include the rolling or tank-treading motion of biological cells and vesicles due to internally generated forces, and the motion of small chemically reactive droplets and solids on hydrophobic surfaces.[4]

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