Harmonic Generation as a Probe of Dissipation at a Moving Contact Line

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We use the pressure generated by a small-amplitude oscillatory flow to probe the dynamics of moving contact lines. By measuring the Fourier amplitude at harmonics of the applied frequency as a function of the steady-state velocity, we are able to determine the velocity dependence of the excess dissipation caused by the moving contact line. We find that the pressure drop associated with this dissipation scales as a power of the contact-line velocity V as $P_{\rm cap} \propto V^x$, with $x = 0.40 \pm 0.05$. We discuss these results in terms of recent theoretical models.

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Spreading of fluids on solids is important in a wide range of industrial and environmental processes. Examples include the application of coatings and the displacement of one fluid by another in a porous medium. Despite considerable effort, an understanding of these processes has remained elusive. The central unsolved problem is how the contact line, where the fluid interface intersects the solid, advances.

The theoretical difficulty in calculating the dynamics of a contact line is that the usual no-slip boundary condition at the solid surface leads to a logarithmic divergence of the total dissipation.[1] Two mechanisms for removing this singularity have been proposed. (1) When the advancing fluid perfectly wets the solid, a thin precursor film forms ahead of the contact line. The problem then reduces to spreading of a bulk fluid on a fluid film and the logarithmic divergence is cut off at the film thickness.[2] However, spreading of the precursor film is not addressed. (2) If the advancing fluid does not perfectly wet the solid, the fluid interface intersects the solid at a finite "contact angle" θ. Slip is assumed to occur within a length l from the contact line which again acts as a cutoff for the divergence.[1] Recent simulations indicate that slip may occur on molecular scales[3,4] due to the large stress near the contact line.[4]

The typical experimental approach[5,6] has been to evaluate the dissipation through direct optical measurements of the apparent dynamic contact angle θ_d. The interface exerts a capillary force $\gamma\cos\theta_d$ on the contact line, where γ is the interfacial surface tension. On a homogeneous surface there is a well-defined static contact angle θ_s at which this force is balanced by wetting forces on the substrate.[2] There is an additional viscous force F_v on a moving contact line. A dimensionless measure of the contact-line velocity V is the capillary number $\mathrm{Ca} = \mu V/\gamma$, where μ is the viscosity of the advancing fluid. At small Ca, capillary forces dominate viscous effects except within $\sim l$ from the contact line.[1] Thus F_v can be determined from θ_d measured far from the contact line: $F_v = \gamma(\cos\theta_d - \cos\theta_s)$. Heterogeneity on real surfaces leads to contact-angle hysteresis[7-9]—the interface is static over a range of θ from the "receding" angle θ_r to the "advancing" angle θ_a. Disorder also complicates the relation between F_v and θ_d as discussed below.

In this paper we present results of a more sensitive kind of experiment which allows us to accurately determine the scaling of θ with Ca. The capillary pressure drop across the interface $P_{\rm cap}$ is measured as a function of V. In a cylindrical tube of radius R, $P_{\rm cap} = -(2\gamma/R)\cos\theta_d$ at low Ca. Very accurate measurements of $P_{\rm cap}$ and its derivatives with respect to V are made by superimposing a small-amplitude oscillatory flow on a larger steady-state flow and measuring the response. Analogous experiments have been shown to yield[10] precise results for the closely related[9,11] system of a sliding charge-density-wave (CDW) conductor.

The oscillatory flow was generated via a plunger driven at frequency ω by an audio speaker, and coupled to the fluid through a latex membrane. The steady-state flow was varied by raising a reservoir of the advancing fluid. A long, narrow-bore tube (high hydraulic resistance) inserted between the reservoir and the sample guaranteed that the flow rate was constant. Two Omega pressure transducers were used to measure both the pressure and velocity as described elsewhere.[12] The ac output of the transducers was amplified, and the harmonic content measured with several PAR 124 lock-in amplifiers. In this fashion, both the in-plane and out-of-phase components of the pressure with respect to the velocity were determined.

The experiments described below were performed in a 1-mm-diam 30-cm-long Pyrex tube with an interface between a mineral oil and a glycerol-methanol mixture. Both fluids had viscosity $\mu = 25$ cP and the interfacial tension was $\gamma = 15$ dyn/cm. The more wetting glycerol mixture was advanced, and we measured $\theta_a = 65°$ and

$\theta_r = 45°$. This hysteresis indicates disorder on the tube. A mineral-oil-filled tube of 0.5 mm diam in series with the sample tube was used to monitor both the oscillatory and steady-state components of the velocity. In all cases the oscillatory component of the velocity was found to be a pure sine wave at the drive frequency with no measurable harmonics.

The total pressure drop measured in the sample tube is the sum of P_{cap} and P_{vis}, the normal viscous dissipation away from the interface. Our experiments were done at low frequencies ($\omega \ll 100$ Hz) where P_{vis} is given by the steady-state expression $P_{vis} = 8\mu LV/R^2$, where V is the mean velocity of the fluid, and L and R are the tube length and radius. We verified that this linear dependence on V held in the absence of an interface, and that there were no measurable Fourier components of P at harmonics of ω. Thus all nonlinear effects can be attributed to the interface.

When a fluid displacement is imposed on the interface, two types of motion of the meniscus can occur: (1) bowing of the interface with the contact line fixed, and (2) displacement of the entire meniscus. The first type of motion occurs in the region of contact-angle hysteresis where the contact line is pinned.[12] Both types of motion occur when the contact line is depinned. The fraction of each depends on both ω and the value of the steady-state pressure relative to the depinning pressure $P_t = (-2\gamma/R)\cos\theta_a$. Following Dimon, Kushnick, and Stokes,[12] we defined ϵ as the mean displacement of the interface due to bowing. Then the imposed mean ac flow $V_{ac}(\omega) = U_{ac} + d\epsilon/dt$, where U_{ac} is the flow due to contact-line motion at fixed shape. Both ϵ and U_{ac} are directly related to θ_d. Expanding for small ac variations, i.e., θ_{ac}, and Fourier transforming we find

$$V_{ac} = \theta_{ac}(dV_{dc}/d\theta)(1 - i\omega/\omega_c)\,, \tag{1}$$

where $\omega_c = (dV_{dc}/d\theta)/(d\epsilon/d\theta)$ and $d\epsilon/d\theta = R/(1+\sin\theta_d)^2$. For $\omega < \omega_c$, the response is in phase with V_{ac} and measurements of P_{cap} directly reflect dissipation at the moving contact line. At higher frequencies, interfacial bowing leads to substantial out-of-phase components. In our experiments, we find $\omega_c \geq 1$ Hz when $\mathrm{Ca} \geq 10^{-5}$.

For measurements at $\omega \ll \omega_c$, the instantaneous pressure drop approximately equals the steady-state pressure $P(V)$ at the instantaneous flow rate V. Treating the oscillatory flow as a small perturbation about the dc flow and making a Taylor-series expansion yields expressions for the Fourier amplitudes A_n at the harmonics $n\omega$ of the drive frequency:

$$\begin{aligned} A_0 &= P(V_{dc}) + \tfrac{1}{4}P''(V_{dc})V_{ac}^2 + \cdots\,, \\ A_1/V_{ac} &= P'(V_{dc}) + \tfrac{1}{8}P'''(V_{dc})V_{ac}^2 + \cdots\,, \\ A_2/V_{ac}^2 &= \tfrac{1}{4}P''(V_{dc}) + \cdots\,, \end{aligned} \tag{2}$$

where primes are used to denote derivatives with respect to velocity. When $V_{dc} \gg V_{ac}$, only the first term on the right-hand side of Eqs. (2) contributes to A_n. Thus the first and second derivatives of the dc P-V relation can be determined by simultaneously measuring V_{ac} and the $n=1$ and 2 components of the pressure response. At small V_{dc}, other terms become important and interpretation of the results is complicated. For $V_{dc} < V_{ac}$ the interface is pinned for part of the cycle and there is a substantial out-of-phase component due to bowing.[13] Note that P_{vis} only contributes to A_1.

Figure 1 presents typical results for A_1/V_{ac} and $-A_2/V_{ac}^2$ at 0.1 Hz. Velocity is converted to Ca on the abscissa to eliminate trivial dependences on μ, γ, etc. The value of V_{ac} for these results corresponds to a peak-to-peak variation in Ca of 2×10^{-5}. Note that the in-phase response decreases when Ca is less than half this value. At the same time the out-of-phase response rises rapidly from zero. These changes reflect pinning of the contact line and the resultant bowing. At higher Ca, motion of the contact line dominates the displacement, and variations in the plotted quantities reflect the first two derivatives of P_{cap} with respect to V. For Ca greater than 2×10^{-4}, A_1/V_{ac} appears to flatten out and $-A_2/V_{ac}^2$ appears to go to zero. As discussed below, this may reflect a crossover in the nature of the contact-line motion.[9]

Our main goal is determination of the exponent x relating $P_{cap} - P_t$ to Ca:

$$(R/2\gamma)(P_{cap} - P_t) = \cos\theta_d - \cos\theta_a = B\,\mathrm{Ca}^x\,. \tag{3}$$

In this dimensionless form, any trivial dependence of B and x is removed. The exponents relating Ca to P'_{cap} and P''_{cap} are $x-1$ and $x-2$, respectively. Thus the decrease of both A_1 and A_2 in Fig. 1 indicates $x < 1$. To make a quantitative determination, the contribution to $P'(V)$ from P_{vis} was measured without an interface and subtracted from A_1/V_{ac}. The remainder was scaled by $R/2\gamma$ and is plotted versus Ca in a log-log plot in Fig. 2.

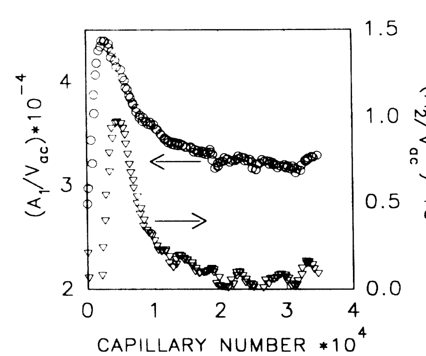

FIG. 1. Dependence of the in-phase components of A_1/V_{ac} and $-A_2/V_{ac}^2$ on Ca, for an ac flow at 0.1 Hz with peak-to-peak amplitude corresponding to $\mathrm{Ca} = 2\times10^{-5}$. For dc flows larger than the ac flow, the in-phase components equal P' and $P''/4$.

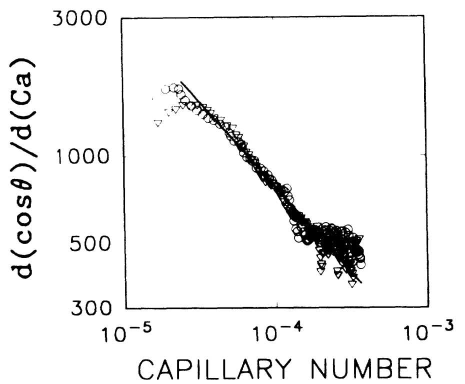

FIG. 2. Scaling of the first derivative of $\cos\theta_d$ with respect to Ca. The solid line indicates a power-law fit. Two data sets represent two ac amplitudes: circles, 2×10^{-5}; triangles, 4×10^{-5}.

For a little more than a decade the results fall on a straight line with slope -0.60 ± 0.05. This leads to a value for x of 0.40 ± 0.05 and $B=3.1\pm1$. For completeness we have also verified that A_2/V_{ac}^2 scales in a consistent manner. Finally, these results are also consistent with previous dc measurements where the error bars are much larger.[14]

Most theoretical work has focused on the velocity dependence of θ_d on homogeneous surfaces. Using asymptotic analysis, Cox[15] found a relationship between Ca and θ_d measured a distance R from the contact line: $g(\theta_d,\lambda)=g(\theta_0,\lambda)+\mathrm{Ca}[\ln(R/l)+Q]$, where g is a simple analytic function, θ_0 is the actual angle of contact at lengths less than l, λ is the viscosity ratio, and Q is a model-dependent constant. Recent simulations for simple fluids[4] are consistent with this expression with $\theta_0=\theta_s$. Since the derivative of g is finite for $\theta>0$, these results imply $x=1$ for a partially wetting fluid on a homogeneous surface.

Several recent papers[16-18] have considered how disorder affects θ_d. Although disorder leads to nonuniform motion of the contact line, Jansons[19] has shown that sufficiently far from the contact line the interface translates uniformly. If D is the scale of the heterogeneity, then uniform motion occurs at scales much greater than D/Ca. Two approaches have been suggested for calculating how θ_d at these scales depends on the nonuniform motion at smaller scales: Zhou and Sheng[16] concentrate on the dissipation due to capillary waves excited on the moving interface, and Raphael and de Gennes[18] and Joanny and Robbins[17] have independently considered a model where velocity-dependent sampling of the surface heterogeneity plays the dominant role. The results from each model are briefly described below.

Zhou and Sheng assume that the contact line rapidly jumps between (say) peaks on a rough surface. The dissipation due to the induced deformation of the interface is then calculated using bulk capillary-wave theory. For typical experimental situations the capillary waves are overdamped and their theory predicts $x=\frac{1}{2}$. Estimates of B span the experimental range but recent work indicates that B is velocity dependent.[16] More work is needed to establish when the rapid-jump approximation is valid.

The alternative approach[17,18] begins by assuming $x=1$ on a uniform surface and that heterogeneity only occurs on scales larger than l. Then the local equation of motion for each region of the contact line can be constructed from the wetting forces, the surface tension, and the dissipation for a contact line moving at the local velocity. One finds that the contact line moves at different velocities over regions with different wetting properties. The time-averaged wetting force is velocity dependent and determines the value of x. To make the calculations tractable artificial periodic heterogenity was considered, yielding $x=\frac{2}{3}$ at constant velocity. By analogy with CDW systems, which show similar velocity-dependent effects,[11] one expects a lower exponent for surfaces with random heterogeneity.

In these latter calculations, θ_d approaches the value for a homogeneous surface with average wetting properties when $|\cos\theta_d-\cos\theta_a|>|\cos\theta_a-\cos\theta_r|$. Our measured hysteresis corresponds to a range in $\cos\theta$ of 0.3 and the data in Fig. 2 do suggest a crossover to $x=1$ in this region. More work on surfaces with different amounts of contact-angle hysteresis will be important in determining which of the theoretical treatments of roughness is correct. They would also rule out alternative explanations for x due to nonlinear effects on a uniform substrate. Possible examples of such effects are variations in surface tension along the interface due to varying surfactant concentrations, or non-Newtonian behavior near the contact line due to the high stress.

In conclusion, we have studied the dynamics of a moving fluid-fluid interface using a novel technique, i.e., by measuring the harmonic content of the response of the system to a small-amplitude oscillatory flow superimposed on a steady-state flow. This allows us to characterize the nonlinear pressure-velocity relation of a moving contact line. The results are inconsistent with current understanding of motion on a uniform substrate. However, the measured exponent, $x=0.40\pm0.05$, is near the values expected from simple calculations for heterogeneous subtrates. More work is needed to establish the universality of this exponent and the underlying mechanisms which determine it.

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