Spreading of thin films assisted by thermal fluctuations

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We study the spreading of viscous drops on a solid substrate, taking into account the effects of thermal fluctuations in the fluid momentum. A nonlinear stochastic lubrication equation is derived, and studied using numerical simulations and scaling analysis. We show that asymptotically spreading drops admit self-similar shapes, whose average radii can increase at rates much faster than these predicted by Tanner’s law. We discuss the physical realizability of our results for thin molecular and complex fluid films, and predict that such phenomenon can in principal be observed in various flow geometries.

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Water drops spreading on a table and oil drops lubricating a pan are two common examples of a phenomenon encountered frequently in the kitchen as well as in natural and industrial environments: Spreading of liquids on solid surfaces. Despite its prevalence and the basic hydrodynamic principles involved, it was not until the late 1970’s that the asymptotic rate of spreading processes was found by Tanner \cite{1} for surface-tension dominated flows. The spatial scale $\ell$ of a viscous drop spreading on a smooth plane increases asymptotically in time as $\ell \sim t^2$, where $z = 1/10, 1/7$ for radially symmetric two-dimensional and one-dimensional flow geometries, respectively. This asymptotic response has been found in many molecular and polymeric droplets, whose decreasing thickness has been detected down to 100 nm \cite{2}.

As the field of nano-fluidics is evolving towards formation of thinner and thinner liquid films, theoretical tools are needed to describe flow patterns in such geometries. However, the applicability of classical hydrodynamic theory for these systems is questionable. While the necessity to incorporate van der Waals (vdW) fluid-solid attraction was recognized long ago \cite{3}, other fundamental aspects have never been fully addressed. In particular: Does a three-dimensional hydrodynamic description hold for a film whose thickness is just a few molecular layers? What are the effects of thermal fluctuations on the deterministic hydrodynamics at such small scales?

To resolve these questions, extensive molecular dynamics (MD) or lattice-gas (LG) simulations of flow in liquid films are required to allow comparison and quantify deviations from a regular hydrodynamic theory \cite{4}. While a full resolution of these questions is still not available within current computational possibilities, a few recent studies are indicative. For example, Abraham et al. \cite{5} used LG algorithm to study flow in a precursor film associated with a spreading drop, and demonstrated significant deviations from the predictions of a hydrodynamic model \cite{6}. On the other hand, MD simulations of nanojets, whose initial radius was around 10 molecular diameters, were shown to be qualitatively consistent with simulations of a stochastic Navier-Stokes (NS) equation, where the viscous stress tensor was supplemented by a stochastic tensor whose temperature-dependent magnitude is determined from the fluctuation-dissipation theorem \cite{7}. The emerging picture is that, at least in some cases, a hydrodynamic description can still be used as a quantitative tool in studying flow of nano-fluids, however modifications of the classical equations are required.

In this Letter we take one further step forward by exploring the influence of thermal fluctuations on the shape and rate of spreading of nano-dimension drops, while assuming a generalized NS equation holds, similarly to \cite{8}. We should note, however, that in addition to thermal fluctuations other modifications of the hydrodynamic equations that stem from density variations near the interfaces \cite{9}, might be necessary in this regime.

Let us start by considering the dynamics of the height $h(x, y, t)$ of an infinite incompressible planar viscous fluid film on top of a smooth solid surface, located at $h = 0$, as depicted in Fig 1. We consider highly viscous fluids, such that inertia can be neglected. The mass conserving dynamics of long wave length fluctuations of the surface, $|\nabla h| \ll 1$, is described by the lubrication equation

\begin{equation}
\frac{\partial h}{\partial t} = \frac{1}{3\eta} \nabla \cdot (h^3 \nabla p), \tag{1}
\end{equation}

where $\eta$ is the viscosity and $p$ is the pressure. The derivation of Eq. (1) from the NS equation is a standard exercise in fluid mechanics \cite{8}. Spatial variations of the pressure associated with fluctuations of the liquid-vapor interface result from several sources: gravity, surface tension, and VdW attraction with the solid surface:

\begin{equation}
p = \rho gh - \gamma \nabla^2 h + A/h^3, \tag{2}
\end{equation}

where $\rho$ is the fluid density, $g$ is the gravitational acceleration, $\gamma$ is the liquid-vapor surface tension, and $A$ is the Hamaker constant. Tanner’s law corresponds to similarity solutions of Eq. (1)

\begin{equation}
h(\bar{x}, t) = |x|^{-\beta} f(|x|/t^2) \tag{3}
\end{equation}

in the surface-tension-dominated regime $|\gamma \nabla^2 h| \gg |\rho gh|, |A/h^3|$, where the exponent $\beta = 1, 2$ is determined
by requiring volume conservation $V = \int d^d\vec{x} h(\vec{x}, t)$, yielding $\beta = 1$ for one-dimensional ($d = 1$) and $\beta = 2$ for two-dimensional ($d = 2$) flow geometries, respectively.

The central equation of this paper is a stochastic generalization of Eq. (1):

$$\frac{\partial h}{\partial t} = \frac{1}{3\eta} \nabla \cdot (h^3 \nabla p) + \frac{2k_BT}{3\eta} \nabla \cdot [h^{3/2}\xi(\vec{x}, t)] , \quad (4)$$

which captures effects of thermal fluctuations on the surface dynamics. Here, $\xi(\vec{x}, t)$ is a spatio-temporal Gaussian white noise. Principally, Eq. (4) can be derived from the full three-dimensional NS equation, similarly to Eq. (1), by adding a stochastic stress, representing thermal fluctuations of the fluid momentum, to the viscous stress tensor $\eta$. We can avoid however such a tedious derivation by considering a reduced, linear version of Eq. (4), and use the fluctuation-dissipation theorem to find the correct magnitude of thermal fluctuations of the fluid momentum, to the viscous stress tensor $\eta$. Namely, the linear eigenmodes of the stochastic surface dynamics are required to satisfy:

$$\Gamma_\eta \frac{\partial \delta h_{\vec{q}}}{\partial t} + p_{\vec{q}} = \sqrt{2\Gamma_\eta k_BT} \, \xi_{\vec{q}}(t) , \quad (5)$$

where $p_{\vec{q}} = (pg + \gamma|q|^2 - 3A/H^4)\delta_h \cos(\vec{q}\cdot\vec{x})$ is the pressure (mechanical energy density) of a surface eigenmode, $\Gamma_\eta = 3\eta/|q|^2H^3$ is its friction coefficient, and $\xi_{\vec{q}}(t)$ is the spatial Fourier transform of $\xi(\vec{x}, t)$. Notice that the long wavelength approximation underlying Eq. (4) implies $|q|H \ll 1$. Dividing both sides of Eq. (5) by $\Gamma_\eta$ and taking the inverse Fourier transform we obtain:

$$\frac{\partial \delta h}{\partial t} = \frac{1}{3\eta} \nabla \cdot (H^3 \nabla p) + \frac{2k_BT H^3}{3\eta} \nabla \cdot [h^{3/2}\xi(\vec{x}, t)] . \quad (6)$$

The linear Eq. (6) describes near equilibrium thermal fluctuations of a surface, $|\delta h| \ll H$. The spreading dynamics of a drop that does not satisfy this condition must be described by a nonlinear equation. To this end, notice that Eq. (6) can be recovered from the deterministic part of Eq. (6) by making the transformation $H, \delta h \to h$ and requiring the resulting equation to conserve fluid mass. By following exactly the same steps the nonlinear Langevin Eq. (4) can be derived from Eq. (6).

A word of caution is in order here. As for any extrapolation of the fluctuation-dissipation theorem to non-linear, far from equilibrium dynamics, a local equilibrium assumption must be made. Namely, the description of the surface dynamics with Eq. (4) assumes that the magnitude of thermal fluctuations of the liquid-vapor interface at $\vec{x}$ is determined solely by the local value of the surface height $h(\vec{x}, t)$. This assumption is justified only for thermal fluctuations whose wavelength

$\lambda \ll \lambda^*(\vec{x}, t) = h/|\nabla h|$. The relaxation dynamics of fluctuations whose wavelength $\lambda > \lambda^*(\vec{x}, t)$ is strongly coupled to interface fluctuations, and thus their magnitude cannot be assumed to be given by the near-equilibrium result [4]. Including these modes in the stochastic analysis involves advanced methods [10], and will not be pursued here. Since we expect $\lambda^*(\vec{x}, t) \to \infty$ as $t \to \infty$, our local equilibrium assumption becomes asymptotically correct. In addition, the number of linear eigenmodes with $\lambda > \lambda^*$ scales as $(\lambda^*/L)^d-1$, where $L$ is the lateral size of the drop. Therefore, we expect Eq. (4) to provide a better description of the pre-asymptotic dynamics in two-dimensional than in one-dimensional geometries.

In studying Eq. (4), our basic motivation was to understand the possible effects thermal fluctuations may have on the asymptotic rates of spreading, e.g. by modifying Tanner’s law. With this view, we focused our analysis on two characteristic flow geometries: (i) one-dimensional drops confined in a channel of width $W$ (Fig. 1), and (ii) two-dimensional radially symmetric drops. In the first case, Eq. (4) assumes the form:

$$\frac{\partial h}{\partial t} = -\frac{\gamma}{3\eta} \frac{\partial}{\partial x} (h^3 \frac{\partial h}{\partial x}) + \frac{2k_BT}{3\eta W} \frac{\partial}{\partial x} [h^{3/2}\xi(x,t)] . \quad (7)$$

In the second case, Eq. (4) becomes:

$$\frac{\partial h}{\partial t} = -\frac{\gamma}{3\eta r} \frac{1}{r} \frac{\partial}{\partial r} \left[ r h^3 \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial h}{\partial r} \right) \right] + \frac{2k_BT}{3\eta} \frac{1}{r} \frac{\partial}{\partial r} [h^{3/2}r^{1/2}\xi(r,t)] . \quad (8)$$

We simulated the volume-conserving spreading of a drop dominated by the dynamics (7) by using finite-difference-based computational techniques as in [11], which guarantee non-negativity of the field $h(x,t)$ for the deterministic part of Eq. (7). In our simulations, the noise term is included in the RHS of a spatial-temporal discrete version of Eq. (7), which is advanced in time through an implicit method. Non-negativity of $h(x,t)$ is physically implemented by a short-range repulsive potential between the liquid and the solid substrate, which in principle should be included in the pressure in Eq. (4). We avoid the explicit use of such a potential, by allowing numerical noise realizations only if they preserve non-negativity of $h(x,t)$. Such a procedure induces correlations in the otherwise white noise field, which are unavoidable if the repulsive potential is not introduced explicitly. In our simulations
we use a non-dimensional version of Eq. (7):

\[ \frac{\partial \tilde{h}}{\partial t} = -\frac{\partial}{\partial \tilde{x}} (\tilde{h}^{3} \frac{\partial \tilde{h}}{\partial \tilde{x}^{3}}) + \sqrt{2\sigma} \frac{\partial}{\partial \tilde{x}} \left[ \tilde{h}^{3/2} \xi(\tilde{x}, \tilde{t}) \right], \tag{9} \]

where \( \tilde{h} = h/h_{0} \), \( \tilde{x} = x/h_{0} \), \( \tilde{t} = t/t_{0} \), where \( h_{0} \) is the maximal height of the initial drop, \( t_{0} = 3\eta h_{0}/\gamma \), and \( \sigma = k_{B}T/\gamma h_{0} \). Our initial condition is a one-dimensional droplet with circular cross section, and a substrate wet by a precursor film of height \( \xi(\tilde{x}, \tilde{t}) \) is the earlier is the deviation from Tanner’s to dimensional variables, we obtain that the stochastic force \( \sigma \partial \tilde{h} / \partial \tilde{x} \) is dominant on the RHS of Eq. (9) \[ \tilde{h} \sim \frac{1}{\sqrt{T/\gamma}} \]. By contrast, if the stochastic force is dominant we consider a self-similar solution of the form \( \tilde{h} = \tilde{h}(\tilde{x}/\tilde{t}^{1/2}) \). Thus, we obtain \( \tilde{h} \sim \sqrt{T/\gamma} \) over a time interval \( \tilde{t} \) and space interval \( \tilde{x} \). Thus we obtain \( \tilde{h} \sim \sqrt{T/\gamma} \), in agreement with the asymptotic behavior of our simulation. Assuming the scaling relations \( \tilde{h} \sim |\tilde{x}|^{-1} \) and \( \tilde{t} \sim |\tilde{x}|^{4} \) we evaluate the surface tension term in Eq. (9) as \( |\tilde{x}|^{-8} \) and the average of the stochastic force as \( \sqrt{2\sigma |\tilde{x}|^{-5}} \). Requiring dominance of the stochastic term and returning to dimensional variables, we obtain that the stochastic scaling behavior is expected in the regime

\[ |x| \gg x^{*}, \quad h \ll h_{0}^{2}/x^{*}, \tag{11} \]

\[ x^{*} = \tilde{h}_{0}^{7/6}W^{1/6}/\ell_{T}^{1/3} \] and \[ \ell_{T} = \sqrt{k_{B}T/\gamma} \]. Thus, a necessary condition for observation of stochastic scaling behavior is \( h_{0} \gg W \gg \ell_{T} \). Typical values of \( \ell_{T} \) are few angstroms for molecular fluids (far from the critical
point), or colloid size for colloidal suspensions \[14\]. Applying similar analysis for the radially symmetric spreading, Eq. 8, shows that in this case self-similarity dominated by the stochastic force gives rise to an enhanced rate of spreading \( \ell_{\text{stoch}} \sim \tilde{t}^{1/6} \), compared to Tanner’s law \( \ell_{\text{det}} \sim \tilde{t}^{1/10} \). The average stochastic force is dominant over surface tension if

\[
r \gg h_0^{1/3} / \ell_T^{1/3}, \quad h \ll h_0^{2/3} / \ell_T^{1/3},
\]

and thus requires \( h_0 \gg \ell_T \).

For molecular fluids, the enhanced rates associated with stochastic scaling behavior can be observed if the stochastic force in Eq. 9 is dominant not only with respect to the surface tension term as is expressed in Eqs. 11, but also with respect to the VdW force that can be quite strong for thin films \[13\]. In the nondimensional units of Eq. 9 this force takes the form \( \frac{1}{3} \beta \frac{\partial}{\partial x} (h^{-1} \frac{\partial h}{\partial x}) \). Following a similar approach to the one that led to Eq. 11 we use for one-dimensional geometry the scaling relations \( h \sim |x|^{-1} \) and \( t \sim |x|^4 \) to compare between the average stochastic and VdW forces and obtain the additional condition for the stochastic scaling regime

\[
x \ll h_0^{3/2} / \ell_T^{1/3} / \ell_{VdW}^{2/3} W^{-1/6},
\]

where \( \ell_{VdW} = \sqrt{A / \gamma} \). An overlap between the intervals in Eq. 11 and 13 is achieved if \( h_0 \ll W (\ell_{VdW} / \ell_T)^2 \).

Typical values of \( A \) are \( 100 k_B T \) \[13\] and thus \( \ell_{VdW} > \ell_T \), and this overlap can be obtained for \( h_0 \gg W \gg \ell_T \). Similar analysis for two-dimensional geometry yields the result \( r \ll (h_0^{11} / \ell_T^2 / \ell_{VdW}^4)^{1/3} \). Consistency of this condition with Eq. 13 is possible only if \( h_0 \ll \ell_T^{5} / \ell_{VdW}^4 \), which seems unfeasible for typical fluids. We conclude that volume preserving fluctuations-dominated spreading can be observed for molecular fluids in one-dimensional flows if the initial height of the drop is large enough.

By contrast, for complex fluids VdW forces with the solid plate are not expected to significantly affect the spreading process, and thus we require \( x(r) \ll h_0^2 / a, \quad h \gg a \) for one- and two-dimensional flows, respectively. An overlap with Eqs. 11, 12 is achieved if \( h_0 \gg (a^6 W / \ell_T^2)^{1/5}, a^{3/2} / \ell_T^{1/2} \) for one- and two-dimensional flow geometries, respectively. Both conditions are easily realized if the initial drop is large enough.

Another spreading dynamics in which a stochastic scaling behavior might be observed is a "leaking" process, in which the height of the film at \( x = 0 \) is fixed to a constant value \( h_0 \) by a continuous supply of fluid. A self-similar dynamics in this case has the form \( \tilde{t} \) with \( \beta = 0 \). Following similar analysis we obtain for one-dimensional geometry the scaling behaviors: \( \ell_{\text{det}} \sim \tilde{t}^{1/4}, \quad \ell_{\text{stoch}} \sim \tilde{t}^{1/3} \), while for two-dimensional geometry both \( \ell_{\text{det}} \) and \( \ell_{\text{stoch}} \) \( \sim \tilde{t}^{1/4} \). For the one-dimensional geometry we obtain an increased asymptotic rate of spreading due to thermal fluctuations. To check the realizability of the stochastic scaling regime we compare the average stochastic force with surface tension and VdW terms, using the scaling relations: \( h \sim \text{const} \) and \( t \sim \tilde{x}^3 \). For molecular fluids where VdW forces are important the stochastic scaling behavior is expected in the regime \( h_0^{3/2} W^{1/2} / \ell_T \ll x < h_0^{5/2} \ell_T / W^{1/2} \ell_{VdW}^2 \), which is again possible provided \( h_0 \ll W (\ell_{VdW} / \ell_T)^2 \). Stochastic scaling behavior of a complex fluid drop under this condition is achieved if \( h_0 \gg a \) and \( x \gg h_0^{2} W^{1/2} / \ell_T \).

To conclude, we derived a Langevin lubrication equation \( \tilde{t} \), and showed that it gives rise asymptotically to significant deviations from Tanner’s law of spreading. By comparing the average stochastic force with classical forces such as surface tension and Van der Waals, we showed that fluctuation-assisted spreading is expected asymptotically in various flow geometries of molecular and complex fluids. Complex fluids are attractive candidates for studying this phenomenon, since confocal microscopy techniques enable direct observation of macroscopic thermal effects in systems such as colloidal suspensions. Direct imaging of thermal capillary waves of an interface between two colloidal liquids was recently achieved by such methods \[14\], and we believe that similar tools may enable observation of the enhanced rate of spreading predicted in this letter. We hope that this result, together with other examples, will motivate further studies of the role of thermal fluctuations in small dimensional fluid systems.

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