Contact angle of evaporating drops of completely wetting liquids

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The spreading of evaporating droplets without a pinned contact line is studied experimentally and theoretically, measuring the radius $R(t)$ of completely wetting alkane drops of different volatility on glass. Initially the drop spreads ($R$ increases), then owing to evaporation reverses direction and recedes with an almost constant non-zero contact angle $\theta \propto \beta^{1/3}$, where $\beta$ measures the rate of evaporation; eventually the drop vanishes at a finite-time singularity. Our theory, based on a first-principles hydrodynamic description, well reproduces the dynamics of $R$ and the value of $\theta$ during retraction. Finally we show the volatility dependence of the contact angle can be understood within a thermodynamic approach.

The evaporation of liquid drops, in the form of dew, rain, or mist generated by breaking waves, must be accounted for accurately in the heat and mass balance of climate models. Evaporation is also important for industrial processes such as spray drying or ink jet printing. As a result, the evaporation of droplets has attracted a great deal of attention over the past few years (for recent reviews see [1–3]).

The two situations most studied are (i) the "coffee-stain" problem in which a drop is deposited on a rough substrate to which its contact line remains anchored during evaporation [4, 5] and (ii) droplets of completely wetting liquids deposited on a perfectly smooth surface [6–8]. The latter problem, studied here, has attracted a great deal of attention since it is unclear why a completely wetting liquid exhibits a non-zero contact angle during evaporation [9, 10]. This problem is difficult because it involves diverging viscous stresses and evaporation rates, which need to be regularized to predict the motion [11, 12]. In doing so, the shape of the droplet is a priori unknown and has to be calculated; however this requires the prediction of the speed of the moving contact line, which is due to a complicated interplay between pinning, thermal activation and viscous dissipation [13, 14]. In addition, numerous secondary effects can arise from evaporation such as buoyant convection [15], Kelvin effects (curvature dependence of the equilibrium vapor pressure) [16, 17] or non-uniform temperatures. The latter may lead to Marangoni flows (driven by surface tension gradients) [18].

Here we study the relative effect of evaporation and spreading systematically by placing completely wetting droplets of alkanes (pentane (C$_5$H$_{12}$) to nonane (C$_9$H$_{20}$)), whose volatility varies by two orders of magnitude, on a clean glass surface (see Fig. [1]). The perfectly circular drop shape indicates that contact line pinning is not important. Our drops are sufficiently small, so that convection in the gas phase is negligible, and the evaporation rate is limited by vapor diffusion into the surrounding gas phase. Moreover, our drops are flat which limits temperature gradients such that the system can be assumed isothermal, especially for alkanes that do not evaporate too fast [19].

Previous studies have found that the contact angle of such a completely wetting but evaporating droplet can be nonzero [6, 8, 15, 20, 21]. As already mentioned, the interpretation of such a non-zero contact angle for a completely wetting liquid, which we denote by $\theta_{ev}$, is difficult, since it represents a fundamentally non-equilibrium situation. The presence of stress and evaporative singularities at the contact line, which need to be regularized on a microscopic scale, make the problem inherently multi-scale [11, 12, 22]. As a result, the value of $\theta_{ev}$ of an evaporating drops has remained a subject of debate. The time dependence of the drop radius is also intriguing. Since the fluid is wetting it starts to spread, but at some point, the evaporation starts to dominate, the drop retracts and $R$ eventually vanishes at time $t_0$.

Experiments were performed by gently depositing a drop on a flat glass surface using a microsyringe, and recording its weight and shape using a precision balance.
and a drop shape analyzer (Kruss Easydrop), from which the radius $R$, height $h$, volume $V$, and apparent contact angle $\theta$ are extracted. The alkanes used were ultra pure, from Sigma-Aldrich, the substrate were glass microscope slides, cleaned with sulfonchroomic acid and piranha solution. The equilibrium vapor pressure $P_{\text{sat}}$ of the different alkanes varies over two orders of magnitude, while the macroscopic contact angle is thus controlled by evaporation, the time derivative in (3) is neglected, demonstrating that evaporation must be included into the description of the contact line dynamics itself, rather than including it phenomenologically.

To do better, one needs to solve the viscous flow problem in the drop coupled to the evaporation which is limited by the diffusion of vapor. Pouliard et al. [8] proposed a model based on scaling arguments, which qualitatively reproduced their experimental observation. However, a fully self-consistent description of the coupled problem [12] relieves the evaporative singularity by the presence of van der Waals forces, which inhibit evaporation. In the lubrication approximation, the equations of motion are:

$$\dot{V} = -4\beta R,$$

where $\beta$ is the evaporation parameter [12]. Solving the resulting differential equation for $V$, and substituting back into Tanner’s law to find $R$, we find

$$R \propto \left[\int_0^{11/10} - t^{11/10}\right]^{3/7} t^{1/10}. \tag{2}$$

Fig. 3 shows (2) as the dot-dashed line, with both a pre-factor and $t_0$ as an adjustable parameter. Clearly, this simple theory is unable to describe the drop dynamics satisfactorily, demonstrating that evaporation must be included into the description of the contact line dynamics itself.

In the lubrication approximation, the equations of motion are:

$$\frac{\partial h}{\partial t} + \frac{\gamma}{\eta r} \frac{\partial}{\partial r} \left[ h^3 \frac{\partial}{\partial r} \left( \frac{\partial^2 h}{\partial r^2} + \frac{1}{r} \frac{\partial h}{\partial r} + \frac{a^2}{h^3} \right) \right] = -j_{\text{ev}}, \tag{3}$$

where $a = (A/6\pi\gamma)^{1/2}$ is a microscopic length that originates from van der Waals forces ($A$ is the Hamaker constant), and $h_f$ is the thickness of the microscopic wetting film. The kernel is given by

$$K(r, r') = \frac{2}{\pi} \left\{ r \left[ K(r'/r) - E(r'/r) \right], \quad r' < r \right\} + \left\{ r' \left[ K(r/r') - E(r/r') \right], \quad r' > r \right\} \tag{4}$$

where $K$ and $E$ are the complete elliptic integrals. Using a quasi-static approach, which means that when considering evaporation, the time derivative in [3] is neglected, [22] derives an effective evaporative contact angle

$$\theta_{\text{ev}} = k \left( \frac{\eta \beta}{\gamma a^{1/2} R^{1/2}} \right)^{1/3}. \tag{5}$$
where \( k \) is a constant of order unity \[19\]. Motion is such that the contact angle \( \theta \) is driven toward \( \theta_{ev} \) according to the Cox-Voinov law \[23\]:

\[
\dot{R} = \frac{\gamma}{9B\eta} \left( \frac{4V}{\pi R^3} \right)^3 \theta_{ev}^3,
\]

where \( B \) is the usual logarithmic molecular cutoff also present without evaporation \[19\].

The equations (1), (5), (6) derived here are the same as the scaling analysis proposed in \[8\]; however because of this analysis they were unable to calculate the prefactors. As a result, they could not predict quantitatively the drop dynamics, but only check power laws. Here we have done the full analysis; we were able to introduce an evaporative cutoff by including the effect disjoining pressure consistently.

We have simulated the complete equations of motion (3), (4) with parameters that lie in the quasi-static regime, and compared it to the model (1), (5), (6) in Fig. 4 (lengths are rescaled with the initial drop radius \( R_0 \) and time with \( R_0\eta/\gamma \)). The constant \( k \) has been fitted, everything else can be determined without further adjustment. The model shows a very good agreement with the simulation.

Now comparing the model to experimental data, we measure the evaporation parameter \( \beta \) using (1) and estimate \( a \approx 4 \) \( \text{Å} \) using Lifshitz theory \[24\]; \( B \) in (6) is estimated to vary between 1.43 and 1.70 and use an intermediate value of 1.62 for all our experiments.

Figs. 3 and 5 compares \( R(t) \) between model and data for various alkanes. We find excellent agreement for slowly evaporating alkanes: heptane to nonane, cf. Fig. 5 (a). In addition, the macroscopic contact angle \( \theta \) is also well described by these equations, and approaches a constant steady state value at late times (inset Fig. 5 (a)). For pentane and hexane, for which evaporation is dominant, the drop hardly spreads and the contact line recedes very quickly, see Fig. 5 (b). This means \( \partial h/\partial t \) is not small, and the quasistatic assumption, which is the basis of our model, breaks down \[19\]. As a result, the model is only able to reproduce these dynamics qualitatively, as it overestimate the spreading motion at short times. In addition, as these drops evaporate very quickly, the isothermal assumption may also be breaking down.

As for the contact angle, breakdown of the quasistatic assumption means that the measured angle is not necessarily the same as \( \theta_{ev} \) given by (5), which also has a weak dependence on the drop radius. Nevertheless, plot-
good agreement with experiment during both spreading and retraction phases of the experiment. We explain the counterintuitive observation that a completely wetting liquid can have a finite contact angle when evaporating, and calculate its dependence on the evaporation rate using thermodynamic arguments.

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[19] See Supplemental Material at [URL will be inserted by publisher] for a critical discussion on the assumptions, theoretical expressions for the prefactors $k$ and $B$ and details on the parameters in the model.