Stains Arising from Dried Liquid Drops

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Introduction

When liquid droplets containing dispersed solid material dry on a solid surface they leave the solid material as a deposit. The pattern of this deposit has important implications for many printing, cleaning and coating processes. In this paper a new computational model is described for modeling deposits left by liquid drops that dry by evaporation and (or) by the absorption of the liquid into a porous substrate. The model includes fluid-dynamics influenced by surface tension, phase change, and heat transfer processes, which are all found to be important for the deposition pattern of the solid material.

A classic example of one type of deposit is the “coffee-ring” problem in which a ring stain is formed along the perimeter of a patch of spilled coffee. This type of ring deposit is shown to develop as a consequence of surface-tension driven flows resulting from evaporation of liquid, particularly at the drop’s perimeter. One requirement for ring formation is that the contact line at the edge of a drop must be pinned. The present model is based on the assumption that pinning occurs because of evaporation-driven dynamics in the vicinity of the contact line. A computational study is presented to show how this happens. It will also be shown that the formation of a ring deposit does not occur in all situations. For example, in sufficiently small drops the flow of liquid to the edge of the drop may be too slow and evaporation too fast to cause a build-up of solids before the drop is completely evaporated.

An excellent reference for experimental observations of coffee-ring formation, including a proposed explanation of the phenomena can be found in the paper by Deegan, et al [1]. There it was observed that evaporating drops appear to be pinned at their outer edge. With this constraint, surface tension causes a mean flow of fluid toward the drop’s edge to compensate for a change in curvature resulting from evaporation at the drop’s surface. This flow (see Figure1) carries suspended solid material to the edge where it is deposited in a narrow ring.

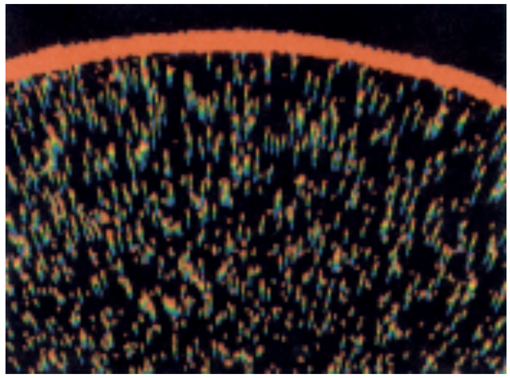

Figure 1. Multiple exposure of moving particles showing flow toward edge of drop [1].

The explanation proposed by Deegan, et al [1], is not quite complete: for example, they do not include any thermodynamic considerations necessary for evaporation, nor do they elaborate on why the edges of their drops are pinned. In the following we describe a computational model that supports the basic mechanism proposed by Deegan, et al [1], but also addresses these additional issues that are important for the formation of coffee-ring stains.

Predicting the Deposition Patterns of Suspended Solids in Evaporating Drops

The present model is built on the shoulders of a commercial computational-fluid-dynamics (CFD) package, ***FLOW-3D***® that provides a Navier-Stokes solver for fluid dynamics in the presence of free liquid surfaces, heat transfer, and many other features [2]. To represent both suspended solid material in the liquid and deposited solid material on a substrate, we have introduced two scalar concentrations for these quantities. The suspended mass density is specified with respect to the volume of fluid within a computational volume element, while the deposited solids mass density is with respect to the entire element volume. This distinction is necessary to allow the liquid to evaporate while leaving a solid deposit. The suspended solids move with the liquid. Deposited solids, which can only form on solid surfaces, do not move.

Evaporation at a liquid surface concentrates the suspended solid. Should this density reach the close-packing density for the solids, and if there is an adjacent surface for deposition, the suspended solid is immediately converted to stationary (deposited) solid. Initial concentrations of suspended solids, however, are typically very low (e.g., of order 1% or less [1]). This means that there would have to be almost complete evaporation before the density of the suspended solid reaches the close-packing limit and is deposited. An alternative mechanism is needed.

We propose that deposition occurs at contact lines in the presence of evaporation. To test this hypothesis we have computed the flow in the vicinity of a contact line with a 15° static contact angle. The liquid is water initially at 20°C and evaporation occurs at the liquid surface under the assumption that the surrounding air has a constant saturation temperature of 4°C. Evaporation rapidly cools the liquid at its surface because of the removal of the heat of vaporization, but the solid surface at the contact line is assumed to remain at a constant temperature of 20°C and heats the liquid in that region by conduction. As a consequence evaporation is greatest in the vicinity of the contact line, which causes a net flow of liquid towards the contact line. This produces a local concentration of suspended solid where the liquid is completely evaporating and results in deposited material on the solid surface. Figure 2 shows a snapshot of this flow process, where marker particles are used to visualize in a qualitative way the movement of suspended solid. In this figure the height of the channel containing the liquid is 15μm. A solid surface is at the bottom where the liquid forms a contact angle of 15° under static conditions. The top boundary is a plane of symmetry. The manner in which the ***FLOW-3D***® program is able to model dynamic contact lines without specifying a location or contact angle has been discussed in previous coating meetings [3] and will not be repeated here.

Figure 2 shows how suspended solid is likely to be deposited on the substrate because of evaporation. In our stain model we assume that the amount of deposition at a contact line during one time step is equal to the amount of dispersed solid in the volume of liquid that has evaporated in the control element containing the contact line during the time step.

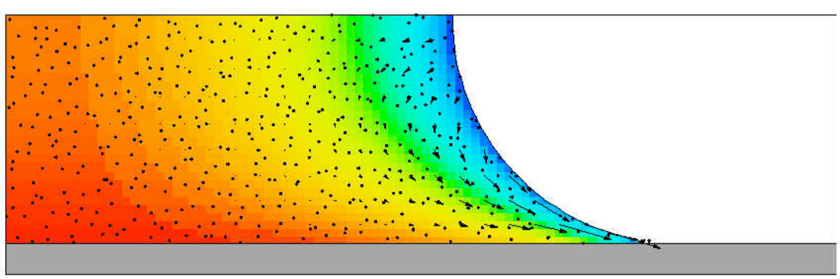

Figure 2. Simulation of flow generated at a contact line by evaporation. Marker particles pile up at contact line where the evaporation is greatest. Only every third flow vector is plotted near the contact line to reduce clutter.

This mechanism of deposition explains why evaporating drops become pinned at their edges. Once some material is deposited at the contact line this increases the effective length of the contact line (similar to a rough surface) and increases the force holding the liquid at that location. Subsequent deposition only serves to further increase the pinning force. Pinning forces associated with deposited material have not yet been incorporated into the computational model presented here; instead a different technique has been used to pin the drop edge for our initial study.

Test Example One – Large Drop

The drops studied in reference 1 had a nominal diameter of 8mm. For our first test example we consider a slightly larger spherical-cap water drop with maximum thickness of 1mm and radius of 0.89cm. To "pin" the outer edge of the drop at its initial radius the static contact angle was set to zero degrees for all radii less than 0.89cm and to 170° (i.e., non-wetting) for all larger radii. By this mechanism the drop retained its initial radius for the entire vaporization time. The initial density of suspended solid was 0.001g/cc (volume fraction of 0.00053). Only one quarter of the 3D cap was modeled (because of symmetry) using 6 grid cells in the thickness and 40x40 grid cells to cover the horizontal extent.

The initial drop and substrate temperatures were 20°C. A very dry background saturation temperature of 1°C was used with a phase change accommodation coefficient of 0.5. In this case phase change is essentially controlled by the conduction of heat in the liquid. In fact, if no heat is added to the drop from the substrate or from heat transfer with the surrounding air, the drop very quickly reaches the saturation temperature of the air and no further evaporation is possible.

With simple heat conduction from the substrate, which was held at a constant value of 20°C, the drop required a little more than 40s to completely evaporate. Figure 3 shows that the computed deposition of solid material at the end of evaporation. A "coffee ring" of solid deposit has indeed formed at the initial location of the drop's edge. In this plot a red color corresponds to any deposit density greater than 0.1gm/cc (i.e., 100 times the initial density). Some variation in deposition is observed around the periphery, which is probably caused by the discreteness inherent in the computation.

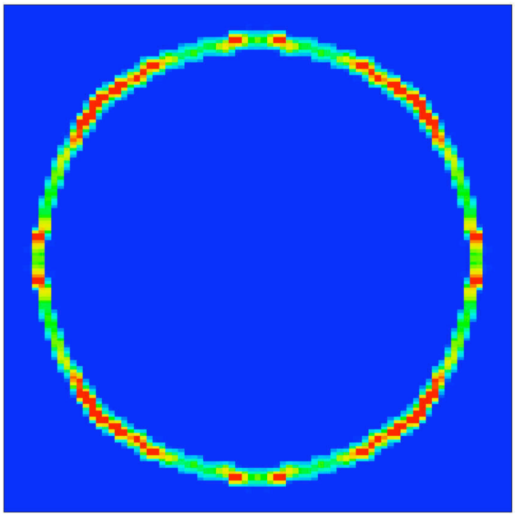

Figure 3. Computed coffee ring stain for large drop.

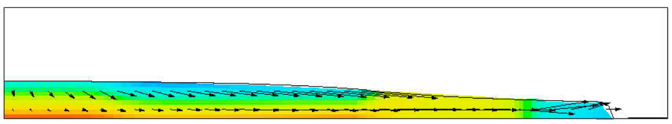

Figure 4. Vertical cross section from center to edge of drop at 17s. Flow toward outer edge is clearly evident.

The computations are in agreement with observations: there is a mean flow of liquid toward the perimeter of the drop, Fig.4, and evaporation is greatest in the neighborhood of the contact line. Deposition of solid material at the contact line because of evaporation is the origin of the characteristic “coffee ring” stain.

Test Example Two – Small Drop

One advantage of computational simulations is that once a model is established it is easy to investigate the consequences of changing physical parameters. For example, if we reduce the drop size significantly does a ring stain still form? To answer this question we reduced the size of the previous drop by a 100, to a radius of 0.0089cm and a thickness of 0.001cm. Also, for a more efficient computation, cylindrical symmetry was assumed, but the same general resolution of 6 grid cells in the thickness direction and 40 radial cells was maintained.

In this test the liquid almost completely evaporated in 25ms. Although surface tension was attempting to direct flow toward the edge of the drop where evaporation is greatest, the total evaporation time was too short for any significant deposit to form at the edge. In fact, the edge evaporated so quickly that it did not even remain pinned. Essentially the final deposit (stain) distribution closely followed what would be expected if the solids simply settled vertically onto the substrate surface, with most at the center where the drop was thickest and least at the edge.

This dependence on drop size should not be surprising. Evaporation depends on the conduction of heat from the substrate to the surface of the drop. The time for heat conduction to penetrate the thickness of the drop is proportional to the square of the thickness. Therefore, the small drop being 100 times smaller than the large drop is roughly evaporating 10^4 times faster.

Summary

This is a work in progress. Much remains to be done to understand the deposition patterns created by evaporating drops. Having a model to experiment with offers a great advantage for uncovering the parameters that offer the greatest potential for controlling the deposition. For instance, Deegan, et al [1] suggested that it might be possible to control the deposition of suspended solid to improve the printing of sharp lines or other patterns. This and other possibilities remain to be explored.

The new model is also applicable to the coating of paper where instead of evaporation, liquid is removed from a liquid film by absorption into a porous substrate (paper) leaving a deposit of suspended solid material on the substrate surface (the coating). In this instance the deposit is treated as a porous layer with it's own flow resistance.

References

1. Deegan, R.D., et all, "Capillary flow as the cause of ring stains from dried liquid drops," Nature **389**, 827 (1997).

2. ***FLOW-3D***® User's Manual, Flow Science, Inc. report FSI-00-1(2000); www.flow3d.com

3. Hirt, C.W., "Direct Computation of Dynamic Contact Angles and Contact Lines," 3rd European Coating Sym. ECS'99, Sept.7-10 (1999); Hirt, C.W. and Brethour, J.M., "Contact Lines on Rough Surfaces with Application to Air Entrainment," proceedings 11th Intn. Coating Sci. and Tech. Sym., Sept. 23-25, 2002, Minneapolis, Minn.