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Simulating the Residue left by Evaporating Drops

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Background

The "coffee ring" effect is the name given to a well known observation where the evaporative drying of a drop of coffee leaves behind a ring of dark material at the edge of the original drop. On first thought one would expect that the coffee particles, which are uniformly distributed in the drop, would simply be deposited uniformly over the area wetted by the drop. It has only been in recent years that researchers have uncovered the mechanisms that produce the ring effect (Deegan, R.D., et al).

As currently understood, the edges of drops can become pinned because of roughness or chemical elements on the surface on which they lie. Heat transfer to the drops from the substrate or the air induces evaporation, which is usually greater near the drop edge. Surface tension forces then adjust the curvature of the remaining liquid consistent with the pinned edge, which results in a net flow of liquid toward the edge. This flow replenishes the evaporative loss but also moves solute to the edge where it is concentrated by evaporation. Eventually, this mechanism builds up a ring deposit of solute at the original edge of the drop.

The residue from dried drops has implications for many useful applications, including general coating processes, formation of pixel arrays of organic materials for video displays and for a variety of micro-electro-mechanical (MEMS) devices.

Because many factors control the distribution of dried residue it is desirable to have some means to model the fluid dynamics of the process to aid engineers in making the best choices for each specific application. Such a capability has been incorporated into ***FLOW-3D***[1] making it possible to computationally investigate the influence of such parameters as the initial solute concentration, fluid viscosity, volatility of the solvent, evaporation rate, surface tension and initial shape of the drop.

This technical note presents a brief description of the residue formation model and illustrates it with several computations of an evaporating drop subject to different physical conditions.

Residue Modeling

[1] ***FLOW-3D*** is a registered trademark in the United States and other countries.

FLOW-3D is a general purpose computational fluid dynamic program that includes all of the features needed for evaporation of liquid drops. What is new is the addition of the capability to leave a solid residue after liquid in a region has evaporated. It also has been necessary to add a capability to approximate a pinned contact line in order to concentrate residue at a fixed drop edge.

Two scalar variables are used to model residue formation. One is the macroscopic mass density of solute in a fluid. This scalar flows with the fluid and occupies some volume fraction of the solute-solvent mixture. A second scalar is used to record solid deposition, the "residue," and does not move with the fluid; it remains fixed wherever it is formed. This scalar is automatically defined when the residue model is activated by setting IRESID=1 in the *prepin* input file as well as defining the macroscopic density of the residue. In practice, there can be more than one scalar that leaves a deposit, but only the total deposit of all scalars is recorded by the single residue scalar. This model only works in the context of one-fluid, free-surface situations.

When solute is deposited there is a transfer of scalar concentrations from the moving solute to the non-moving deposited solute.

As the liquid evaporates, the residue concentration increases. A maximum concentration (or packing density) RMXSC(*ns*) is defined for each solute scalar #*ns*. The residue starts forming at locations where a solute reaches its maximum concentration. By default, the maximum solute concentration density is an unrealistic large number.

The mental picture here is that the excess solute density represents the material sticking out of the liquid, since only the maximum close packing density can exist within the liquid. It is the quantity sticking out that is transferred to the stationary residue scalar. Once the liquid has been completely evaporated, then all the solute will have been transferred to the residue.

The value of the scalar variable representing solute in a liquid is the macroscopic density of the solute. The volume fraction of solute in a mixture of solute and solvent is the macroscopic density divided by the microscopic density of the solute. In the residue model the maximum packing density, RMXSC(*ns*), may be a little smaller than the microscopic solute density if the dried residue has some porosity.

Several attempts were made to pin the contact lines. In these attempts it was imagined that pinning was caused by subscale roughness which would increase the adhesion surface area and reduce the contact angle. Unfortunately, these attempts were not very successful, probably because the phenomenon is not resolvable, and because it was localized to a region that was no larger than a single mesh cell. The contact line could oscillate about the pinning point and introduce excessive noise in the computations. A different technique was then used that worked quite well. This consisted of the use of a "phantom" obstacle surrounding the initial drop and extending vertically upward to the top of the grid, forming a cylindrical wall around the droplet, with the radius equal to the initial droplet radius. Within the phantom component the permittivity is zero so that fluid

cannot penetrate the space occupied by it, however, as with any phantom components, there are no area or volume blockages. Because it has no solid surfaces the phantom obstacle does not alter the surface-tension wall adhesion forces. With this component in place the contact angle for the fluid is set to a low (wetting) value, e.g., 0.0. Effectively, the low contact angle makes the fluid want to move outward, but it is restrained by the phantom obstacle's zero permittivity, creating the net effect of a pinned contact line.

Illustrative Examples

For a base case to illustrate the residue model a spherical cap drop was selected having the radius of 89 μm and height 5 μm.* The material is toluene with density of 967 kg/m^3, viscosity 2.022 Pa-s, thermal conductivity 0.129 Watt/m/K, specific heat 1645 Joule/kg/K and surface tension coefficient 0.033 N/m. The contact angle of 10 degrees was deemed small enough to maintain a pinned contact line.

The solute had a microscopic density of 1875 kg/m^3 with a close packing density of 1162.5kg/m^3 corresponding to porosity of 38% in the packed material. The initial concentration of solute was 0.10 kg/m^3, or 5.33% by volume

The phase change model assumed a heat of vaporization of 4.06e+5 J/kg and an accommodation coefficient of 0.05. The saturation temperature of the surrounding atmosphere was 293° K, which was also the initial temperature of the liquid, so the system is initially in thermal equilibrium. Heating of the drop was through the substrate temperature that could be varied. For the base case the temperature of the substrate was 303.0° K (30° C or 10° C above equilibrium) and the heat transfer coefficient between the liquid and the substrate was 9.723e+3 W/m^2.

The computational model for the base case consisted of an axisymmetric mesh of 50 radial cells spanning 60 μm and 7 axial cells spanning 8 μm. A smaller than average axial cell size of 0.5 μm was used at the substrate to improve the resolution of the viscous shear stress at the bottom surface. This turned out to be important because enough vertical resolution is needed to allow for the outward radial flow of solute caused by surface tension forces. Without this resolution a significant coffee ring does not form.

Base Case

A cross section of the initial drop and grid is shown in Fig.1a. Complete drying of the drop occurred after 0.038 s and a coffee-ring type of residue was formed as seen in Fig.1b, which shows the radial distribution of macroscopic residue density (i.e., the residue scalar values). The maximum residue height at the ring is 422 nm, while in the central region it is 172 nm. These values are computed by dividing the scalar value by the packing density (1162.5) and multiplying by the vertical height of the cell containing the scalar (0.5 μm). If the residue were uniformly distributed over the initial area of the drop, then the average height would be 298 nm (or a uniform residue scalar value of 0.694).

* In the text SI units are used, but the actual computation was performed using CGS units with degrees K.

Finally, Fig.1c shows a 3D image of the residue that has been magnified by a factor of 30 in the vertical direction. The light source is not able to highlight the surface shape in this case very well, probably because of the magnification (a problem that will have to be corrected in the future).

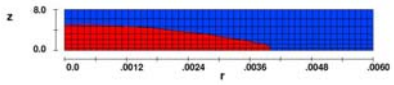

Figure 1a. Cross section of initial drop (r>0).

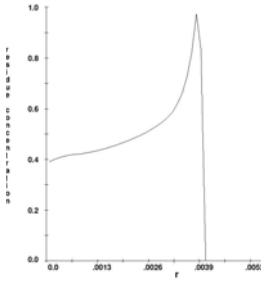

Figure 1b. Residue profile of Base Case.

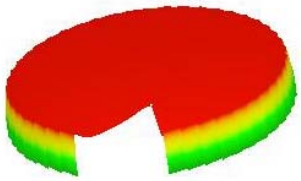

Figure 1c. 3D view of residue magnified 30 times, with 60° cutout.

Base Case with Increased Viscosity

A repeat of the Base Case was done with a tenfold increase in the value of the liquid viscosity. The time required to dry out was the same as in the base case, 0.038 s. As expected, increasing the resistance to flow reduces the coffee-ring effect, Fig.2a. The maximum height is 316 nm and the minimum in the center is 203 nm. This is seen in the comparison of the radial distribution of the residue, Fig.2c, with that of the Base Case and with the next case to be discussed, which had a greater substrate temperature.

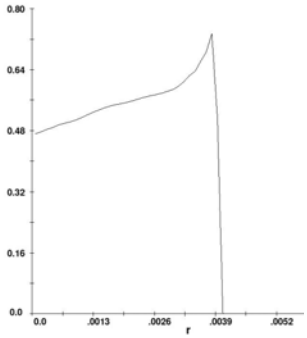

Figure 2a. Residue with higher viscosity.

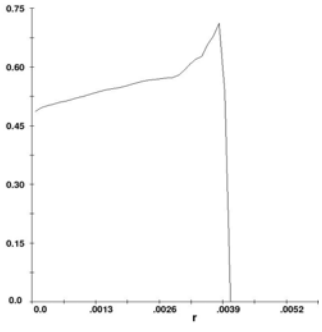

Figure 2b. Residue with higher temperature.

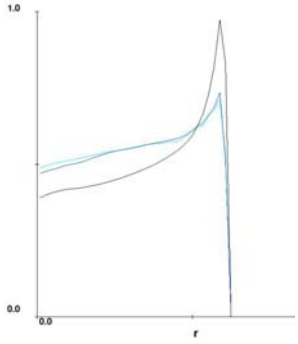

Figure 2c. Residue comparisons with base case (highest peak). High viscosity and high temperature cases are nearly the same.

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Base Case with Higher Substrate Temperature

Keeping the viscosity at the original value for the Base Case, but increasing the substrate temperature by 50° C to 80° C, reduces the time to dry out from 0.038 s to 0.007 s. With less time to transport solute to the edge of the drop we would expect to see a smaller coffee-ring effect. That is exactly what happens as seen in Fig2.b. The maximum residue height is 305 nm, while the central value is 211 nm. A comparison of the more viscous and hotter cases with the Base Case, Fig.2c shows that hot and viscous cases result in very similar residue deposits, and both have a much less pronounced ring distribution.

Base Case with more Viscosity and Higher Temperature

When both the higher viscosity and higher heating rate are applied to the drop the ring-like residue distribution is completely suppressed as shown in Fig.3. Here there is a weak maximum residue height of about 307 nm at about four tenths of the radius from the center. Essentially the residue depth is close to the expected uniform value of 298 nm. The dry out time is nearly equal to that for the previous 80° C case.

Base Case with Slower Evaporation

Based on the previous results, we would expect to have a larger coffee-ring effect if we lengthen the dry out time, which would provide more time to transport solute to the edge of the drop. A simple way to increase the dry out time is to reduce the phase-change accommodation coefficient, in this case from 0.05 to 0.005. With all other parameters the same as in the Base Case, the dry out time increased from 0.038 s to 0.052 s. A sharper and slightly higher residue ring is formed, as seen in a comparison with the Base Case in Fig.4. The maximum height is 447 nm and the central height is 176 nm.

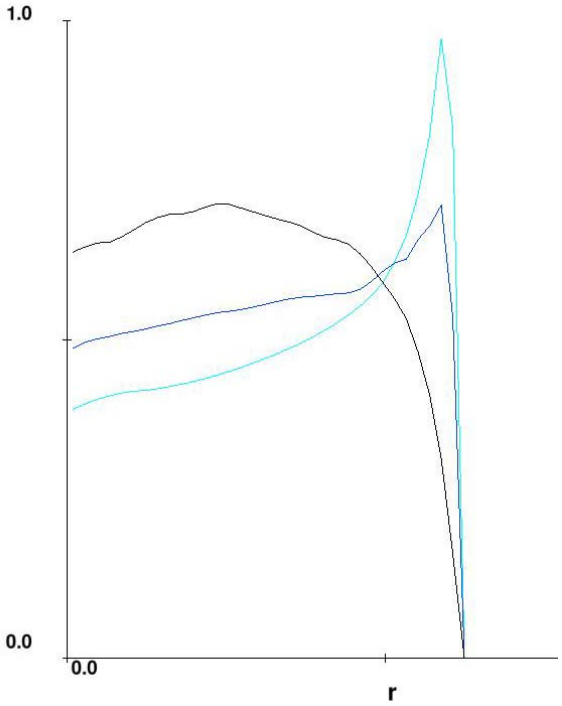

Figure 3. Residue with higher viscosity and heating rate (highest at axis) compared with Base case (maximum peak) and higher viscous case (lower peak).

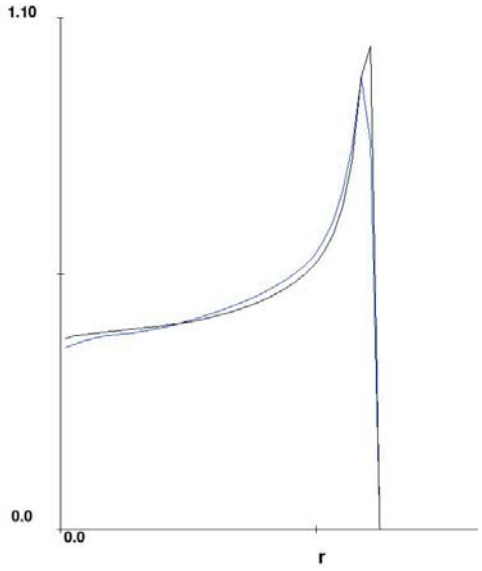

Figure 4. Residue of Base Case (lowest peak) compared with slow evaporation case, which has a somewhat higher peak and sharper ring.

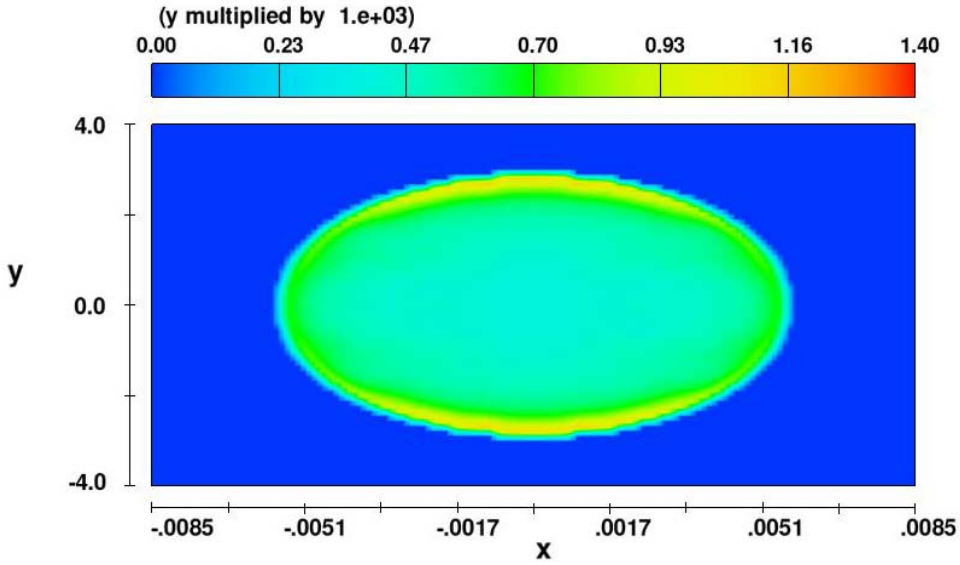

Figure 5. Non-uniform residue distribution on substrate from an initial elliptical drop.

Non-Circular Drop

As a final example, the Base Case drop was distorted into an elliptical shape whose width is twice the height. All other parameters were the same as in the base case. Because the fluid volume and heating rate are the same, the dry out time remains 0.038 s, equal to that in the Base Case. There is a ring-type residue; however, a greater amount of residue collects at the longest sides with the smallest curvature, Fig.5. This may be because there is less flow resistance in reaching the sides closest to the bulk liquid and solute.

Overlapping Drops

It is useful to note that the phantom component method of pinning the contact line worked well in this fully three-dimensional simulation. The phantom component idea can also be used for two overlapping drops that are pinned and cannot flow together into a single drop.

As an example, the Base Case drop was initialized by shifting its center approximately a half radius along the x axis and then assuming symmetry across both the x and y axes. Figure 6a-6b shows the resulting residue distribution on the substrate. Maximum residue accumulates at the boundary between the two drops. It appears that this occurs because residue on the outer portions of the contact line is spread over a larger length and perhaps because viscous stresses reduce the flow to the more remote sections of the contact line. This result appears contrary to experimental results (Deegan, R.D., et al) that indicate greater residue concentrations in regions of positive curvature and less where there is negative curvature. However, in the present case there isn't any negative curvature of the contact line only a cusp at the boundary of the two drops. More work is needed to resolve this issue.

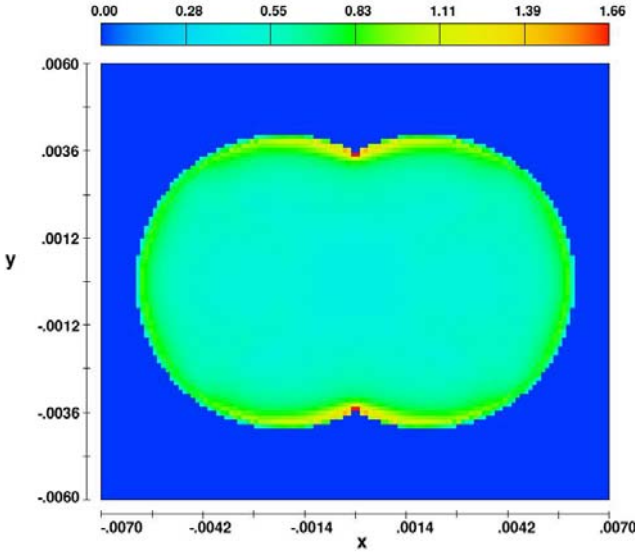

Figure 6a. Residue on substrate for overlapping drops.

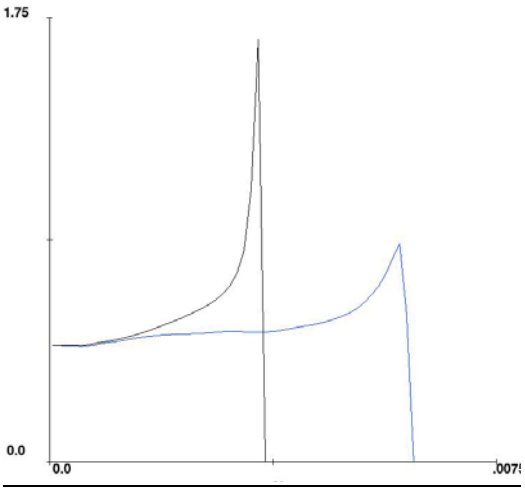

Figure 6b. Residue distribution along x and y axes. Maximum peak is on y axis.

Concluding Remarks

The new evaporation-generated residue model in ***FLOW-3D*** has been described and illustrated with several examples of an evaporating micro-drop of toluene containing a distributed solid solute. The examples show that the model is capable of investigating the effects resulting from variations in many physical parameters defining the drop and its environment.

Refinements that are included in ***FLOW-3D***, but have not yet been used in connection with evaporating drops, are a temperature-dependent surface tension coefficient and viscosity changes caused by the solute concentration changes. Other possible variations might involve non-uniform heating in the substrate or heating by an energy beam (using an available user customization of the main program).

References

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

Addendum: Hints for plotting residue results

The standard ***FLOW-3D*** postprocessor, up through version 9.2, is not well suited to display results of these residue simulations. The principal reason for this is that the postprocessor is generally meant to plot fluid and solid regions, but a residue is something left in an open (non-solid) region when the fluid has been removed. The postprocessor will have additional options for residue plotting, but until that is available the following discussion explains how plots can be made.

Probe results and one-dimensional plots showing the residue density can be made with the standard postprocessor. It must be remembered, however, that the residue is usually less than one mesh cell in height and generally exists on a solid surface.

In two-dimensional plots residue density can be shown by color shading. Because it is often isolated in a single layer of cells, it may be best to use the Advanced option of "No contour smoothing" for those plots. Also, it is best to select "none" for blanking in the Advanced options.

Three-dimensional plots are the most difficult. In this Note the three-dimensional plot results were made by plotting the contour surface of the residue concentration, and shading it with temperature. The contour value for the surface was selected as the minimum value in the residue in order to obtain a plot of the entire surface. Finally, it was necessary to magnify the vertical scale of the plot by a large factor (30 in the plots in this Note). To enter this vertical scaling the user must first request the three-dimension surface plots. Then return to the Analyze tab and go to the Custom plotting option at the left-top corner of the Analyze window. Select the flsinp.tmp file add to it the quantity

vscale=30.0 for a vertical magnification of 30.0. This modified flsinp file can be saved for later use so that the modification will not have to be reentered.

For axisymmetric simulations the postprocessor will at first display only a single slice of the problem in the azimuthal direction since only one mesh cell is used in that direction. By selecting the "tools" option on the tool bar and then the "symmetry" option, the image can be expanded into any azimuthal angle.