Simple analytical model of capillary flow in an evaporating sessile drop

Yuri Yu. Tarasevich*
Astrakhan State University, Tatishcheva 20a, Astrakhan, 414056, Russia
(Received 30 August 2004; published 28 February 2005)

An analytical expression of hydrodynamic potential inside an evaporating sessile drop with pinned contact line is found. The problem is considered for a hemispherical drop (with the contact angle of 90°) at the very early stages of the evaporation process when the shape of the drop is still a hemisphere and the evaporation field is uniform. The capillary flow carries a fluid from the drop apex to the contact line. Comparison with the published calculations performed using lubrication approximation (very thin drop) suggests that qualitative picture of the capillary flow is insensitive to the ratio of initial drop height to the drop radius.

DOI: 10.1103/PhysRevE.71.027301 PACS number(s): 47.55.Dz

I. INTRODUCTION

The desiccated sessile drops attract the attention because of different reasons and possible applications. If a drop of pure liquid dries on a smooth substrate, then the base of the drop shrinks but the contact angle remains fixed. Under evaporation, a drop of colloidal suspension or solution having a strongly anchored three-phase line keeps a spherical-cap shape with a constant base. The contact angle decreases with time, and the height in each point of the profile decreases. To satisfy the anchoring condition, a flow of liquid has to occur inside the drop. An outward flow in a drying drop is produced when the contact line is pinned so that liquid that is removed by evaporation from the edge of the drop must be replenished by a flow of liquid from the interior [1–3]. This flow is capable of transferring 100% of the solute to the contact line and thus accounts for the strong perimeter concentration of many stains. Ring formation in an evaporating sessile drop is a hydrodynamic process in which solids dispersed in the drop are advected to the contact line. After all the liquid evaporates, a ring-shaped deposit is left on the substrate that contains almost all the solute. Perhaps everyone is familar with the dense, ringlike deposit along the perimeter of a dried drop of coffee, tea, milk, or juice on a table.

Exploratory experiments [3] using a variety of carrier fluids, solutes, and substrates indicated that preferential deposition at the contact line is insensitive to a wide range of experimental conditions. Ringlike deposits were observed whenever the surface was partially wet by the fluid irrespective of the chemical composition of the substrate. Different substrates were investigated (metal, polyethylene, roughened Teflon, freshly cleaved mica, ceramic, and silicon). Rings were found in big drops (15 cm) and in small drops (1 mm). They were found with aqueous and nonaqueous (acetone, methanol, toluene, and ethanol) solvents. They were found with solutes ranging in size from the molecular (sugar and dye molecules) to the colloidal (10 μm polystyrene microspheres) and with solute volume fractions ranging from 10^{-6} to 10^{-1}. Likewise, environmental conditions, such as temperature, humidity, and pressure, could be extensively varied without affecting the ring. Effects due to solute diffusion, gravity, electrostatic fields, and surface tension forces are negligible in ring formation.

The vertically averaged radial flow of the fluid in a desiccated sessile drop was calculated in [1]. The conservation of fluid was utilized. A constant evaporation rate all over drop free surface was assumed.

For the case where the limiting rate is the diffusion of the liquid vapor, the evaporation of the drop rapidly attains a steady state so that the diffusion equation reduces to Laplace's equation [3]. In this case the evaporation rate is larger near the contact line and the resulting ringlike deposit is more concentrated at the edge. The models [1,3] deal with the vertically averaged radial flow of the fluid.

In Ref. [4], very thin droplets have been examined ($h_0 \ll R$, where R is the droplet radius and h_0 is the initial droplet height). In this regime, the lubrication approximation can be applied to simplify the governing equations. The streamlines and velocity field were obtained in [4] for nonuniform evaporation of liquid.

Recently, the buckling instability was investigated during the drying of sessile drops of colloidal suspensions or of polymer solutions [5–7]. Drying of a sessile drop of a complex liquid can lead to intriguing complex shapes. Under solvent evaporation, disperse particles or polymers accumulate near the vapor-drop interface. The outer layer of the drop is more concentrated in the polymer and may display a gel or glassy transition and, hence, may form a permeable rigid gelled or glassy skin. This skin behaves like an elastic shell, although it does not block the evaporation. This gelled or glassy skin will, thus, bend as the volume it encloses decreases, leading to large surface distortions.

The processes of skin formation are not the scope of this brief communication. Nevertheless, knowledge of the velocity field inside an evaporating sessile drop is a necessary background to describe the colloidal particle transfer or solute diffusion and skin formation. In Ref. [5], the authors experimentally investigated the conditions under which drop surface buckling occurs and their dependence on the drying rate and contact angle. The contact angle varies in a wide range up to 80°. Obviously, lubrication approximation cannot work in the case of such large contact angles.

*Electronic address: tarasev@astranet.ru

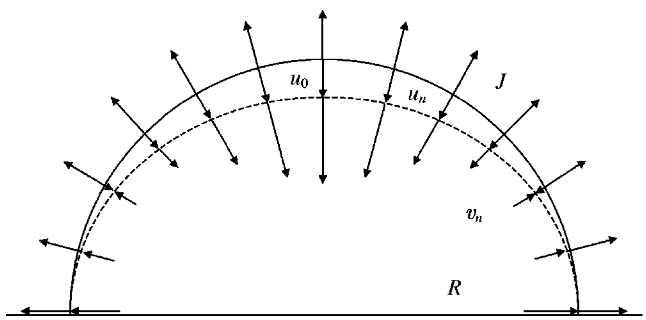

FIG. 1. The solid semicircle represents the initial air-liquid interface of a drop viewed from the side. The dashed line represents a new position of the interface after a very small time dt, if the contact line is pinned. The new position of the interface is a result of the evaporation with the rate J and radial flow of the fluid with the velocity v_n inside the drop. The contact line motion is prevented by an outflow that replenishes the liquid removed from the edge. The drop height decreases with velocity u_0. The volume between initial and new interface position is $dV=\pi R^2 u_0 dt$.

Section II describes how to obtain the space distribution of the fluid flow in the quite different approximation of the very thick drop.

II. MODEL AND RESULTS

Likewise Refs. [1–3] let us suppose that the shape of the drop is a spherical cap. It means that the drop is small, and a spherical cap shape induced by surface tension (Bond number is smaller than one: $\mathrm{Bo}=g(\rho-\rho_f)d^2\sigma^{-1}\ll 1$, where g is gravitational acceleration, ρ is drop density, ρ_f is surrounding medium density, σ is surface tension, d is drop diameter). Let us consider an extremely simple situation when the cap is a hemisphere, i.e., the contact angle is 90°.

Let us suppose that there are a number of dispersed particles inside the droplet. The particle concentration is large enough to produce strong anchoring of the contact line, although it is small enough to consider the fluid as ideal. So, the radius of the contact base between the drop and the solid plate remains constant during drying.

Under evaporation, the height in each point of the profile decreases. Nevertheless, under room conditions, the evaporation is a slow process. For instance, the desiccation time of a 15 mg sessile water drop is larger than 3500 s [8]. This fact gives us the possibility to consider a quasistatic process. We will consider a drop with a fixed free surface and the specific boundary conditions. Quasistatic approximation was utilized in [3] to obtain a vapor rate near the free surface, too.

The conservation of fluid determines the relationship between the velocity of the free surface u_n, the normal to the free surface flow of the fluid v_n, and the rate of mass loss per unit time per unit area of the free surface of the drop by evaporation J

$$\rho v_n + J = \rho u_n.$$

All quantities are supposed the function of the azimuthal angle. (For additional explanations, see Fig. 1.)

Let us consider only the potential flow. The potential of the velocity field φ is a solution of the Laplace's equation

$$\Delta\varphi = 0. \tag{1}$$

The problem of a spherical cap on an impermeable substrate can be replaced by the problem of a lens. Also, we will solve the Laplace's equation inside a spherical area using spherical coordinates.

Measurements of the evolution of the drying drop height h with time t can be performed. Let us suppose, that the velocity of the drop apex, $u_0=u_n(0)$, is known. The mass of the drop is decreasing due to evaporation

$$\int JdS = \rho dV = \rho\pi R^2 u_0 dt,$$

where the integration goes all over the free surface. Let us suppose that the evaporation rate is uniform all over drop free surface, i.e., we will consider only begin of the evaporation. Thus,

$$J = \frac{u_0\rho}{2}.$$

The equation of solute conservation yields

$$v_r|_{r=R} = \left.\frac{\partial\varphi}{\partial r}\right|_{r=R} = u_0\left(\frac{1}{2} - |\cos\theta|\right), \tag{2}$$

where R is the radius of the contact base and $v_r=-v_n$. As mentioned earlier, the problem of a drop is replaced by the problem of a sphere. Presence of the absolute value signs around $\cos(\theta)$ is a result of plane symmetry.

We are looking for the boundary value problem (1), (2) inside a spherical area $(r\leqslant R)$ as

$$\varphi(r,\theta) = \sum_{k=0}^{\infty} A_k\left(\frac{r}{R}\right)^k P_k(\cos\theta), \tag{3}$$

where $P_k(\cos\theta)$ are Legendre polynomials.

Thus,

$$\frac{\partial\varphi}{\partial r} = \sum_{k=0}^{\infty} k\frac{A_k}{R^k}r^{k-1}P_k(\cos\theta). \tag{4}$$

Let us write the right-hand side of Eq. (2) using Fourier-Legendre series expansion also known as a generalized Fourier series expansion

$$u_0\left(\frac{1}{2} - |\cos\theta|\right) = \sum_{k=0}^{\infty} b_k P_k(\cos\theta), \tag{5}$$

where

$$b_k = \frac{2k+1}{2}u_0\int_0^{\pi}\left(\frac{1}{2} - |\cos\theta|\right)P_k(\cos\theta)\sin\theta d\theta.$$

Thus, $b_0=0$, $b_{2k+1}=0$,

$$b_{2k} = u_0(4k+1)\frac{(-1)^k(2k-2)!}{2^{2k}(k-1)!(k+1)!}, \quad k=1,2,\ldots.$$

Taking into account Eq. (2), (4) equals (5), if $r=R$

$$\sum_{k=0}^{\infty} k\frac{A_k}{R^k}R^{k-1}P_k(\cos\theta) = \sum_{k=0}^{\infty} b_k P_k(\cos\theta). \quad (6)$$

Equation (6) is always valid if $A_k = b_k R/k$. Hence, the coefficients of the series (3) are

$$A_{2k} = u_0 R(4k+1)\frac{(-1)^k(2k-2)!}{2^{2k}k!(k+1)!}, \quad k = 1,2, \ldots .$$

The capillary flow carries a fluid from the apex of the drop to the contact line (Fig. 2).

III. DISCUSSION

The key to understanding the pattern formation and buckling instability is the flow profile that is induced inside the evaporating droplet. The velocity field for a hemispherical droplet (Fig. 2) looks almost the same as in the case of very thin drop [4]. It means that the qualitative picture of the capillary flow is insensitive to the ratio h_0/R.

It is quite clear, that more realistic assumption, that a drop has a spherical cap shape with an arbitrary contact angle, cannot change the qualitative picture of the flow. In particular, the calculations of the vertically averaged velocity for the drops with the contact angles up to 90° [1] did not show the qualitative changes of the flow. If a drop has a spherical cap shape with an arbitrary contact angle, then the Laplace's equation can be solved using toroidal coordinates. Although the analytical results are too complicated in this case, numerical calculations should be performed.

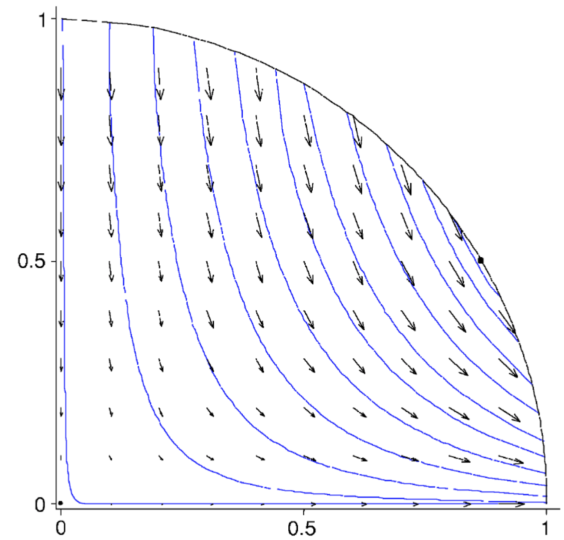

FIG. 2. Velocity vectors and streamlines for a desiccated sessile hemispherical drop with pinned triple line. The evaporation rate is uniform.

The nonuniform evaporation rate cannot change the results qualitatively, but the line, where $v_r(R)=0$, has to move.

[1] F. Parise and C. Allain, J. Phys. II **6**, 1111 (1996).
[2] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, and T. A. Witten, Nature (London) **389**, 827 (1997).
[3] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, and T. A. Witten, Phys. Rev. E **62**, 756 (2000).
[4] B. J. Fischer, Langmuir **18**, 60 (2002).
[5] L. Pauchard and C. Allain, Phys. Rev. E **68**, 052801 (2003).
[6] L. Pauchard and C. Allain, Europhys. Lett. **62**(6), 897 (2003).
[7] L. Pauchard and C. Allain, C. R. Phys. **4**, 231 (2003).
[8] C. C. Annarelli, J. Fornazero, J. Bert, and J. Colombani, Eur. Phys. J. E **5**, 599 (2001).