Evaporating droplets

By NOUSHINE SHAHIDZADEH-BONN[1], SALIMA RAFAÏ[2], AZA AZOUNI[1] AND DANIEL BONN[2,3]

[1]Laboratoire des Matériaux et Structures du Génie Civil, 2 allée Kepler
77420 Champs sur Marne, France

[2]Laboratoire de Physique Statistique de l'ENS, 24 rue Lhomond 75231 Paris Cedex 05, France

[3]Van der Waals-Zeeman institute, University of Amsterdam, Valckenierstraat 65
1018 XE Amsterdam, the Netherlands

The evaporation of droplets on a substrate that is wetting to the liquid is studied. The radius $R(t)$ of the droplet is followed in time until it reaches zero. If the evaporation is purely diffusive, $R \propto \sqrt{t_0 - t}$ is expected, where t_0 is the time at which the droplet vanishes; this is found for organic liquids, but water has a different exponent. We show here that the difference is likely to be due to the fact that water vapour is lighter than air, and the vapour of other liquids more dense. If we carefully confine the water so that a diffusive boundary layer may develop, we retrieve $R(t) \propto \sqrt{t_0 - t}$. On the other hand, if we force convection for an organic liquid, we retrieve the anomalous exponent for water.

1. Introduction

The seemingly simple problem of an evaporating droplet has attracted a great deal of attention (Picknett & Bexon 1977; Birdi, Vu & Winter 1989; Kuz 1991; Parisse & Allain 1996; Deegan et al. 1997; Cachile, Benichou & Cazabat 2002a; Cachile et al. 2002b). It is an appealing problem; in our everyday life we are constantly confronted with evaporating drops and their consequences: it is easy to find the circular deposits left when a drop has dried up, e.g. the dark rings on the coffee table (Parisse & Allain 1996, Deegan et al. 1997). The two situations that have been studied most are droplets deposited on a rough substrate to which the contact line remains fully anchored during the evaporation (Deegan 2000) and droplets of completely wetting liquids deposited on a perfectly smooth and wetting surface for which no contact line anchoring occurs (Cachile et al. 2002a, b).

Both problems are complicated because the form of the droplet during the evaporation is *a priori* unknown, and because of the large number of effects that have to be taken into account. For instance, the evaporation generally leads to a decrease of the temperature within the droplet. This can lead to both a heat flux from the substrate into the droplet, and to Marangoni effects (flows driven by surface tension gradients, if the temperature within the droplet is not uniform (Redon, Brochart-Wyart & Rondelez 1992; Kavehpour, Ovryn & McKinley 2002; Sultan, Boudaoud & Ben Amar 2004). Also, in some cases hydrodynamic flows within the droplet have been observed, and need to be taken into account (Savino & Fico 2004; Deegan et al. 1997).

Here we consider the – at first sight – very simple situation where no contact line pinning occurs. This we do by looking at the evaporation of a perfectly wetting
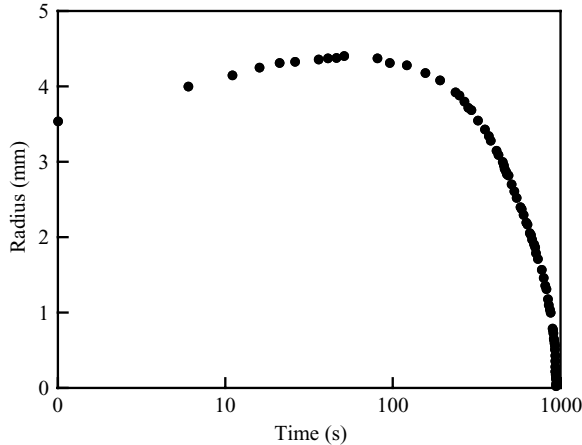
FIGURE 1. Water on mica: droplet radius *vs*. time; the spreading is followed by evaporation.

liquid on a perfectly flat surface: droplets of water and hexane on mica. For wetting liquids such as these two the effects of the anchoring of the contact line are small; we minimize these further by using a surface that is flat at almost the molecular scale. Previous studies have made the interesting observation that the contact angle of such a completely wetting but evaporating droplet can be non-zero (Bourges-Monnier & Shanahan 1995). The interpretation of a non-zero contact angle for a completely wetting liquid is not straightforward, since the equilibrium contact angle is given by the (equilibrium) surface and interfacial tensions in the problem, and it is not clear how to calculate such thermodynamic quantities in a non-equilibrium situation. Consequently, the contact angle of evaporating drops is a subject of debate (Bonn & Meunier 1997).

Closely related to the evolution of the contact angle is the time-dependence of the droplet radius. Figure 1 shows an example for water on mica. On depositing of a drop, since the water is perfectly wetting it starts to spread on the surface and its radius increases in time. However, since the droplet evaporates at the same time, its radius R starts to decrease shortly afterwards, to vanish at a time we denote t_0 (Deegan 2000). Some simple scaling arguments may be used to predict the droplet retraction at late times. Neglecting thermal and Marangoni effects (Davis 1987), it is known that the evaporation rate is proportional to the perimeter of the droplet $dV/dt \propto -2\pi R$ (Deegan *et al.* 1997; M. D. Betterton, M. P. Brenner & H. A. Stone, personal communication), V being the volume of the droplet. Using $V \propto R^2 h$ and considering that the contact angle is constant it follows by integration that $R \propto (t_0 - t)^{1/2}$.

This prediction has been compared with experimental data. In the experiments the evolution of the radius was followed as a function of time for different simple and perfectly wetting liquids having a different volatility. If the data are fitted to a power-law behaviour, $R \propto (t_0 - t)^a$, the values for a that are found are indeed all around 1/2 (Cachile *et al.* 2002a), in agreement with this simple argument.† On the other hand, the value of a reported for water is 0.6; unfortunately, there is no error bar on this exponent as only a single experiment was reported (Deegan 2000). Because of the importance of the evaporation of water droplets, for instance for electricity

---

† They do differ significantly from it in a non-trivial way: the exponents found are slightly smaller than 1/2, the reason for which is still unclear and we will not go into that here.
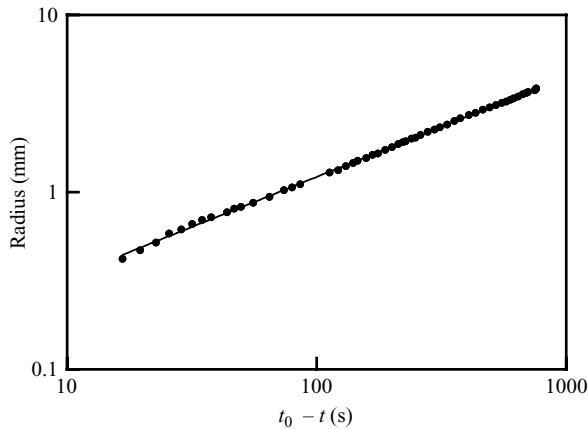
FIGURE 2. Water on mica: a typical log-log plot of the radius as a function of the time to vanishing $R \propto (t_0 - t)^a$; $a = 0.6$.

generation, industrial cooling applications and for the climate, it is important to establish that the difference really exists, and if so, what its causes could be.

To establish that the difference exists, we measured the time evolution of the radius and weight of an evaporating water droplet placed on a freshly cleaved mica substrate. The volume of the droplets was about 1–3 µl; the droplets were gently deposited on the surface using a microsyringe. The largest radius these droplets attained was about 2–3 mm, similar to the capillary length (≈ 2.6 mm). The water used was ultrapure, from a Milli-Q-plus system. Under typical experimental conditions ($T = 20\,^\circ$C relative humidity 40 %), the evaporation rate is about 3×10^{-3} mg s^{-1}. Figure 2 shows a typical log-log plot of the radius as a function of the time to vanishing. The final conclusion from a large number of experiments is that the evaporation can be characterized by: $R(t) = C(t_0 - t)^a$, where R is the radius of the drop, $a = 0.61 \pm 0.03$ (error is one standard deviation) and $C = 0.1 \pm 0.04$. We find that increasing the humidity changes the evaporation rate, but not the exponent a. Similarly, the exponent appears robust to changes in temperature. Effects of aging of the mica surfaces were not observed either. Pinning of the droplets on defects of the substrate was occasionally observed, and leads to non-circular droplets; these experiments have been discarded. It is important to note that our results turn out to be independent of how close they are to the vanishing time t_0 of the drop. Experiments on much smaller droplets followed under the microscope with a rapid camera (125 images s^{-1}) down to the smallest radius of 25 µm show no difference between large and small drops. In other words, there is no evidence from our experiments for a transition between two regimes.

In order to verify that the difference with other experiments does not come from the mica surfaces that we use, we repeated the experiments for a simple liquid: hexane. The result is shown in figure 3, and was again fitted to $R(t) = C(t_0 - t)^a$. Again repeating the experiments a number of times, we obtain an exponent, $a = 0.47 \pm 0.04$, in agreement with previous observations on various organic liquids (Cachile *et al.* 2002*a*).

Simultaneously with the measurement of the radius, we independently determined the mass of the evaporating drop on a balance. This allowed us to verify how the volume scales with the radius. For hexane deposited on mica, we find that the mass scales with $t^{1.5}$, meaning that the volume is proportional to R^3 (figure 4*a*). This is what would be expected if the droplet remained a spherical cap with a constant contact
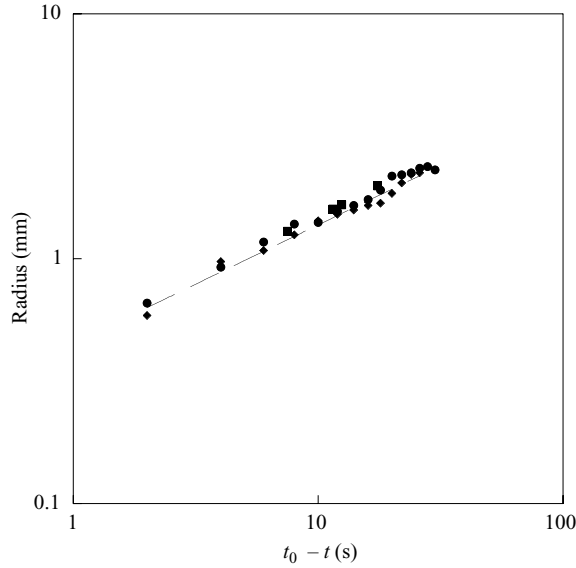
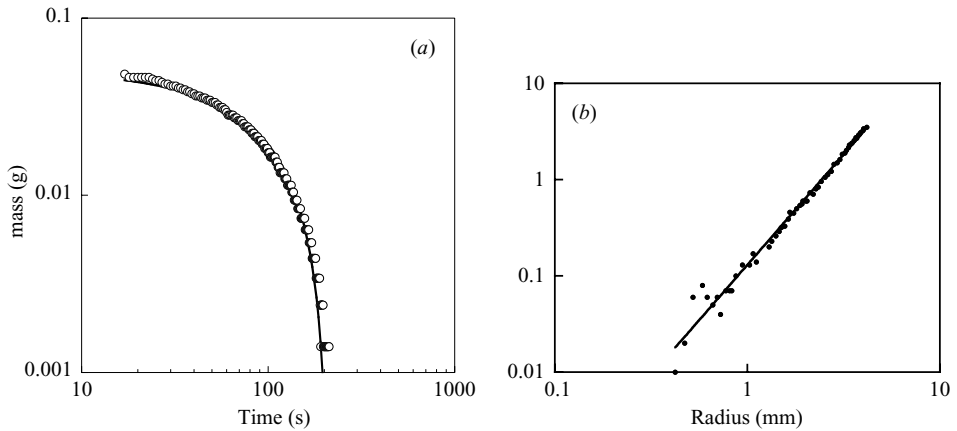FIGURE 3. Evaporation of hexane droplets deposited on mica. $R \propto (t_0 - t)^a$; $a = 0.47$.

FIGURE 4. (*a*) Mass (g) as a function of the time (s) during the evaporation of a hexane droplet deposited on a smooth hydrophilic surface (mica). (*b*) Mass (g) as a function of the radius (mm) during the evaporation of a water droplet deposited on a smooth hydrophilic surface (mica): $M \propto R^{2.3}$.

angle during the evaporation; if this is the case the height scales like the radius and consequently the volume as the third power of the radius. For water, on the other hand, the result is again different. Figure 4 shows that the mass of a water droplet, and consequently the volume, is not proportional to R^3 but to $R^{2.3}$. Although the error bar on the exponent for the vanishing of the mass in time is rather large, due to the rather large uncertainty in the measured weight for small masses, it is evident from the data that the height h decreases much more slowly than the radius R. This implies that the contact angle increases during the evaporation, in sharp contrast with what happens for organic liquids. For the latter the contact angle either remains constant, or decreases somewhat at the final stage of the evaporation. This clearly
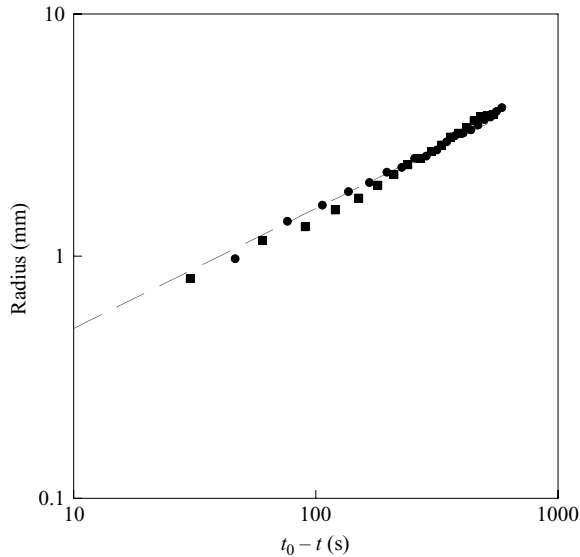
FIGURE 5. Evaporation of a confined evaporating water droplet. $R \propto (t_0 - t)^a$; $a = 0.5$.

shows that besides a difference in the numerical value of the exponent a there is a qualitative difference between the evaporation of water droplets, and droplets of organic liquids. For completeness, we measured the mass of a droplet evaporating on a rough surface of teflon; the contact line is thus anchored and we find that the volume scales as $t^{1.7}$. Contact line pinning can consequently not be at the origin of the different exponent for the vanishing of the mass.

All these results demonstrate that water is anomalous in the sense that its evaporation appears different from that of all other liquids (Cachile *et al.* 2002*a* measured four different alkanes). In addition, the results for water are different from what is expected from our simple scaling argument.

In order to understand the difference, one needs to consider the evaporative flux, which is determined by the undersaturation of the vapour. However, it is unclear whether in general the transport in the vapour phase surrounding the droplet is diffusive or convective. This is perhaps where the difference between water and all the other liquids may lie. Namely, the ideal gas law tells us that at a given pressure, the density of a gas is directly propotional to is molecular weight. The molecular weight of water is $18 \, \text{g mol}^{-1}$, that of air roughly 30 and that of hexane 72. Therefore, water vapour is less dense than air and all other liquids that have been examined have a vapour density that is higher than that of air. The expectation is therefore that the water vapour will rise, leaving unsaturated air around the droplet. The hexane vapour should not rise, and it seems therefore plausible that the air around the hexane droplet is more highly saturated.

In order to test this hypothesis, we performed two experiments. In one, we confined an evaporating water droplet in a small ($1.5 \times 1.5 \times 1.5 \, \text{cm}$) box with only a small opening at the top in order to retain a more highly saturated vapour in the droplet's environment. The result is shown in figure 5. The anomalous exponent disappears: we find $a = 0.53 \pm 0.04$, again from a large number of experiments. On the other hand, we took a standard cooling fan and refreshed the air over an evaporating hexane droplet continuously, by sending and air stream with a velocity of $2 \, \text{m s}^{-1}$ over it. We retrieve

the anomalous exponent for hexane with forced convection: $a = 0.61 \pm 0.04$. These two experiments are in complete agreement with the hypothesis suggested above, and confirm our idea that water evaporation is not simply diffusive.

These experiments also shed some light on the value of the exponent, using the same simple scaling arguments as above. If the evaporation is not controlled by diffusion, there is no longer any reason why the evaporative flux should be proportional to the circumference of the droplet. If convection is important, one would instead expect the rate to be proportional to the surface area of the droplet. This leads to $dV/dt \propto -\pi R^2$. Assuming again a constant contact angle it follows immediately that $R \propto (t_0 - t)$. The exponent 0.6 would then be intermediate between purely diffusive (0.5) and 'convective' (1) behaviour. A quick check on whether this is reasonable can be made by using the fan to force convection on a water droplet; if we do so we find an exponent of 0.7 ± 0.02 shown) confirming this, and showing that indeed there is nothing special about the value of 0.6. Improving on such a simple scaling argument seems a formidable task, and an analytical theory would be difficult. In addition, due to the large separation of length scales between the droplet and the precursor film (that is indeed present on the substrate – see Cachile *et al.* 2002*a*) surrounding it, numerics are very difficult also. This therefore remains an open problem for further study.

The convection is described by the Rayleigh number, which compares buoyancy forces (causing convection) to diffusive and viscous forces (working against it). For our situation, the Rayleigh number can be defined as

$$Ra = \frac{g\Delta\rho/\rho d^3}{\nu D} \tag{1.1}$$

where g is the gravitational acceleration, $\Delta\rho/\rho$ the reduced density difference, ν the kinematic viscosity and D the diffusion coefficient. If we take a $\Delta\rho/\rho$ of 1%, a 1 mm radius drop, $\nu = 10^{-6}\ \mathrm{m^2\,s^{-1}}$ and $D = 10^{-5}\ \mathrm{m^2\,s^{-1}}$, we have $Ra = 10$, which indicates that the onset of convection is close in the experiments. Similarly, a characteristic speed for the convection would be $v = \sqrt{(g\Delta\rho/\rho d)}$ which gives $v = 1\ \mathrm{cm\,s^{-1}}$. All this seems reasonable, and indicates that convection, in the vapour phase, may play a role in the evaporation of water droplets.

REFERENCES

BIRDI, K. S., VU, D. T. & WINTER, A. 1989 A study of the evaporation rates of small water drops placed on a solid surface. *J. Phys. Chem.* **93**, 3702.

BONN, D. & MEUNIER, J. 1997 Evaporation preempts complete wetting – comment. *Europhys. Lett.* **39**, 341.

BOURGES-MONNIER, C. & SHANAHAN, M. E. R. 1995 Influence of evaporation on contact angle. *Langmuir* **11**, 2820.

CACHILE, M., BENICHOU, O. & CAZABAT, A. M. 2002*a* Evaporating droplets of completely wetting liquids. *Langmuir* **18**, 7985.

CACHILE, M., BENICHOU, O., POULARD, C. & CAZABAT, A. M. 2002*b* Evaporating droplets. *Langmuir* **18**, 8070.

DAVIS, S. H. 1987 Thermocapillary instabilities. *Annu. Rev. Fluid Mech.* **19**, 403.

DEEGAN, R. D. 2000 Pattern formation in drying drops. *Phys. Rev.* E **61**, 475.

DEEGAN, R. D., BAKAJIN, O., DUPONT, T. F., HUBER, G., NAGEL, S. R. & WITTEN. T. A. 1997 Capillary flow as the cause of ring stains from dried liquid drops. *Nature* **389**, 827.

KAVEHPOUR, P., OVRYN, B. & MCKINLEY, G. H. 2002 Evaporatively-driven Marangoni instabilities of volatile liquid films spreading on thermally conductive substrates. *Colloids Surf.* A **206**, 409.

KUZ, V. A. 1991 Evaporation of small drops. *J. Appl. Phys.* **69**, 7034.

PARISSE, F. & ALLAIN, C. 1996 Shape changes of colloidal suspensions during drying. *J. Phys. Paris* II **6**, 1111.

PICKNETT, R. G. & BEXON, R. 1977 Evaporation of sessile or pendant drops in still air. *J. Colloid Interface Sci.* **61**, 336.

REDON, C., BROCHART-WYART, F. & RONDELEZ, F. 1992 Festoon instabilities of slightly volatile liquids during spreading. *J. Phys. Paris* II **2**, 1671.

SAVINO, R. & FICO, S. 2004 Transient marangoni convection in hanging evaporating drops. *Phys. Fluids* **16**, 3738.

SULTAN, E., BOUDAOUD, A. & BEN AMAR, M. 2005 Evaporation of thin film: Diffusion of the vapour and marangoni instabilities. *J. Fluid Mech.* **543**, 183.