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On the Effect of an Atmosphere of Nitrogen on the Evaporation of Sessile Droplets of Water

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Summary. The effect of an atmosphere of nitrogen on the evaporation of pinned sessile droplets of water is investigated both experimentally and theoretically.

1 Introduction

When liquid droplets are deposited on a solid substrate in an unsaturated atmosphere they will experience some degree of evaporation. This apparently simple phenomenon is encountered in everyday life as well as in a wide range of physical and biological processes. During the last decade renewed interest in droplet evaporation has been sparked by new developments in applications such as cooling technologies, desalination, painting, DNA synthesis and patterning technologies.

Many studies of the evaporation of sessile droplets have been undertaken, notably those by Picknett and Bexon [6], Bourges-Monnier and Shanahan [1], Deegan [3], Hu and Larson [5], and Popov [7]. The standard theoretical model (hereafter referred to as the "basic model") assumes that the rate-limiting mechanism for evaporation is the diffusive relaxation of the locally saturated vapour at the free surface of the droplet. The basic model decouples the concentration of vapour in the atmosphere from the temperature of the droplet and the substrate, and hence does not account for the effect of the thermal properties of the droplet and the substrate on the evaporation rate. Recently Dunn et al. [4] developed an improved mathematical model for the evaporation of a thin droplet on a thin substrate taking into account the temperature dependence of the saturation concentration of vapour at the free surface of the droplet, and found that its predictions are in reasonable agreement with the experimental results of David et al. [2]. The purpose of the present paper is to build on the progress made by David et al. [2] and Dunn et al. [4] by investigating the effect of an atmosphere of nitrogen on the evaporation of pinned sessile droplets of water both experimentally and theoretically.
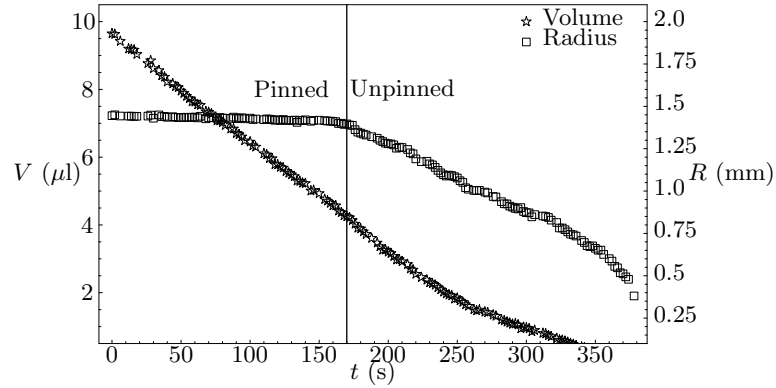
Fig. 1. Typical examples of the experimentally measured evolutions in time of the volume (left hand axis) and the base radius (right hand axis) of a droplet of water on an aluminium substrate evaporating into an atmosphere of nitrogen.

2 Experimental Procedure

The essence of the experiment consisted of depositing a liquid droplet of controlled volume on a substrate and allowing it to evaporate spontaneously. All of the experiments reported here were realised with droplets of pure deionised water resting on four different substrates chosen for their wide range of thermal conductivities, namely aluminium (Al), titanium (Ti), Macor and PTFE. The substrates had dimensions of 10 mm $\times$ 10 mm $\times$ 1 mm (length $\times$ width $\times$ thickness), and their thermal conductivities are given by David et al. [2, Table 2]. In order to contain the ambient gas and to vary the atmospheric pressure, the droplet and the substrate were placed in a "low pressure" chamber. The chamber was cylindrical in shape (105 mm diameter and 95 mm height) with two observation windows and was connected to a gas supply and a vacuum pump. The experimental setup used a DSA100$^{\text{TM}}$ Droplet Shape Analysis (DSA) system from KRÜSS GmbH to monitor the evolutions in time of the volume, contact angle, height and base radius of the droplet. Typical examples of the experimentally measured evolutions of the volume and the base radius are shown in Figure 1. All of the experiments were carried out in a laboratory in which the room temperature was controlled at 295 K with an air-conditioning unit with a precision of ± 1 K. Before each experiment, air was removed from the chamber and replaced with the chosen ambient gas. The pressure of the gas was varied in the range 40 to 1000 mbar. Various ambient gases were used, but, for brevity, only results for an atmosphere of nitrogen are reported here.
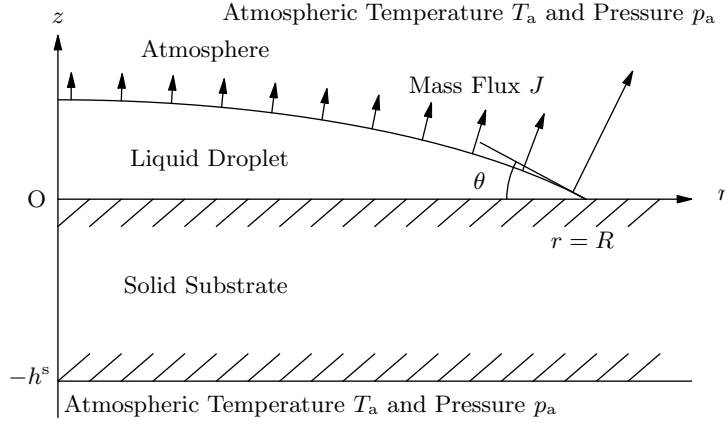
Fig. 2. Geometry of the mathematical model.

3 Mathematical Model

The mathematical model used in the present work represents the quasi-steady diffusion-limited evaporation of an axisymmetric droplet of Newtonian fluid with constant viscosity, density ρ, surface tension γ, and thermal conductivity k resting on a horizontal substrate of constant thickness h^{s} with constant thermal conductivity k^{s}. Referred to cylindrical polar coordinates (r, θ, z) with origin on the substrate at the centre of the droplet with the z axis vertically upwards, the shape of the free surface of the droplet at time t is denoted by $z = h(r, t)$, the upper surface of the substrate by $z = 0$, and the lower surface of the substrate by $z = -h^{\mathrm{s}}$, as shown in Figure 2.

For a sufficiently small droplet whose base radius R is much less than the capillary length $\sqrt{\gamma/\rho g}$, the droplet shape can be approximated as a simple quasi-static spherical cap, and hence the relation between the volume $V = V(t)$ and the contact angle $\theta = \theta(t)$ is given by

$$V = \frac{\pi h_{\mathrm{m}}(3R^2 + h_{\mathrm{m}}^2)}{6}, \tag{1}$$

where $h_{\mathrm{m}} = h_{\mathrm{m}}(t) = h(0, t) = R\tan(\theta/2)$ is the maximum height of the droplet. The total evaporation rate is given by

$$-\frac{\mathrm{d}V}{\mathrm{d}t} = \frac{2\pi}{\rho} \int_0^R J\sqrt{1 + \left(\frac{\partial h}{\partial r}\right)^2}\, r\, \mathrm{d}r, \tag{2}$$

where $J = J(r, t)\,(\geq 0)$ is the local evaporative mass flux from the droplet.

The atmosphere in the chamber surrounding the droplet and the substrate is assumed to be at constant atmospheric temperature T_{a} and atmospheric pressure p_{a}. The temperatures of the droplet and the substrate, denoted by

$T = T(r, z, t)$ and $T^\mathrm{s} = T^\mathrm{s}(r, z, t)$, respectively, satisfy Laplace's equation $\nabla^2 T = \nabla^2 T^\mathrm{s} = 0$. The mass flux from the droplet satisfies the local energy balance $\mathcal{L}J = -k\nabla T \cdot \mathbf{n}$ on $z = h$ for $r < R$, where $\mathcal{L}$ is the latent heat of vaporisation and $\mathbf{n}$ is the unit outward normal to the free surface of the droplet. We assume that the temperature and the heat flux are continuous between the droplet and the substrate, $T = T^\mathrm{s}$ and $-k\partial T/\partial z = -k^\mathrm{s}\partial T^\mathrm{s}/\partial z$ on $z = 0$ for $r < R$, and that the temperature is continuous between the substrate and the atmosphere, $T^\mathrm{s} = T_\mathrm{a}$ on $z = 0$ for $r > R$ and on $z = -h^\mathrm{s}$.

Assuming that transport of vapour in the atmosphere is quasi-static and is solely by diffusion, the concentration of vapour, denoted by $c = c(r, z, t)$, satisfies Laplace's equation $\nabla^2 c = 0$. At the free surface of the droplet we assume that the atmosphere is saturated with vapour and hence $c = c_\mathrm{sat}(T)$ on $z = h$ for $r < R$, where the saturation value of the concentration $c_\mathrm{sat} = c_\mathrm{sat}(T)$ is an increasing function of temperature, approximated quartically in $T_\mathrm{a} - T$ by

$$c_\mathrm{sat}(T) = \sum_{i=0}^{4} \alpha_i (T_\mathrm{a} - T)^i, \tag{3}$$

where the coefficients α_i for $i = 0, \ldots, 4$ were chosen to fit experimental data given by Raznjevic [8], leading to $\alpha_0 = 1.93 \times 10^{-2}$, $\alpha_1 = 1.11 \times 10^{-3}$, $\alpha_2 = 2.78 \times 10^{-5}$, $\alpha_3 = 3.78 \times 10^{-7}$ and $\alpha_4 = 2.59 \times 10^{-9}$ in units of kg m^{-3} K^{-i}. Note that while a simple linear approximation is sufficient for situations with a relatively small evaporative cooling of a few degrees K, such as those considered by David et al. [2] and Dunn et al. [4], the quartic approximation (3) is necessary for situations with a larger evaporative cooling of up to 20 K, such as those considered in the present work. On the dry part of the substrate there is no mass flux, $\partial c/\partial z = 0$ on $z = 0$ for $r > R$, and, since the chamber is much larger than the droplets used in the experiments, far from the droplet the concentration of vapour approaches its far-field value of zero, $c \to 0$ as $(r^2 + z^2)^{1/2} \to \infty$. Once c is known the local evaporative mass flux from the droplet is given by $J = -D\nabla c \cdot \mathbf{n}$ on $z = h$ for $r < R$, where D is the coefficient of diffusion of vapour in the atmosphere. A standard result from the theory of gases is that D is inversely proportional to pressure, and hence we write $D = D_\mathrm{ref}p_\mathrm{ref}/p_\mathrm{a}$, where D_ref denotes the appropriate reference value of D at the reference pressure $p_\mathrm{ref} = 1$ atm. Note that the diffusion coefficient is the only parameter in the model that depends on either the nature of the ambient gas or its pressure p_a.

In the special case $c_\mathrm{sat} \equiv c_\mathrm{sat}(T_\mathrm{a})$, corresponding to $\alpha_i = 0$ for $i = 1, \ldots, 4$ in equation (3), the saturation concentration is constant and we recover the basic model in which the problem for the concentration of vapour in the atmosphere is decoupled from the problem for the temperature of the droplet and the substrate.

The model was solved numerically using the MATLAB-based finite element package COMSOL Multiphysics. The value of D_ref used to obtain the present numerical results was fitted by comparing the experimental results
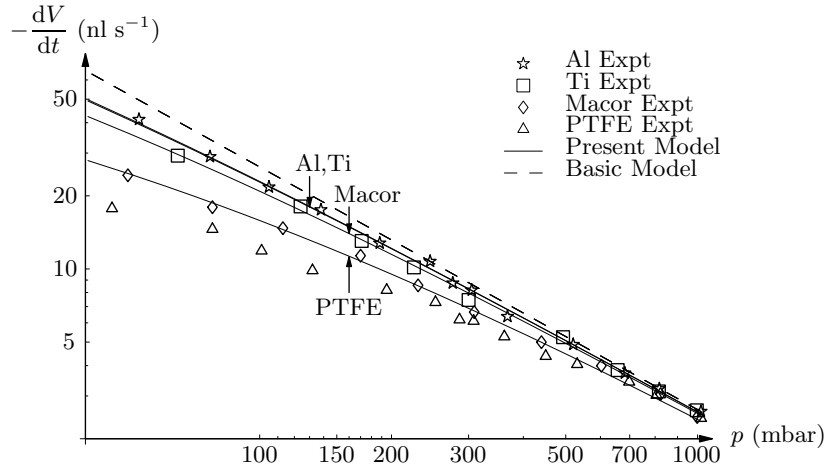
Fig. 3. Experimentally measured evaporation rates of droplets of water in an atmosphere of nitrogen on various substrates for different atmospheric pressures, together with the corresponding theoretical predictions of the mathematical model and the basic model.

for evaporation on an aluminium substrate with the corresponding theoretical predictions. Specifically, for an atmosphere of nitrogen the fitted value of $D_{\mathrm{ref}} = 2.15 \times 10^{-5}$ m^2 s^{-1} differs by less than 15% from the value of $D_{\mathrm{ref}} = 2.47 \times 10^{-5}$ m^2 s^{-1} given by Reid et al. [9], i.e. the difference is comparable with the uncertainty in the theoretical value.

4 Results

As the typical experimentally measured evolutions in time of the volume and the base radius of a droplet shown in Figure 1 illustrate, typically the evaporation process can be divided into two stages. In the first stage, the droplet is pinned and so the base radius is constant while the volume decreases approximately linearly with time. In the second stage, the droplet depins and so the base radius and the volume decrease until complete evaporation. The experimental and theoretical results presented here are for the first stage only, for which the basic model and previous experimental studies (such as, for example, that by David et al. [2]) indicate that the evaporation rate is proportional to the perimeter of the base of the droplet.

Figure 3 shows both the experimental results and the corresponding theoretical predictions of the mathematical model for all four substrates studied for an atmosphere of nitrogen, and shows that the theoretical predictions of the mathematical model using the value of the diffusion coefficient fitted for an aluminium substrate are in reasonable agreement with the experimental

results for the other three substrates studied. Figure 3 also shows the corresponding prediction of the basic model, which are independent of the thermal properties of the droplet and the substrate, which consistently over-predicts the evaporation rate. In particular, Figure 3 shows that for all four substrates studied reducing the atmospheric pressure increases the evaporation rate. Furthermore, Figure 3 also shows that droplets on substrates with higher thermal conductivities evaporate more quickly than those on substrates with lower thermal conductivities. Close inspection of Figure 3 reveals that the agreement between theory and experiment is poorest for the substrate with the lowest thermal conductivity (namely PTFE).

5 Conclusions

An investigation into the effect of an atmosphere of nitrogen on the evaporation of pinned sessile droplets of water has been described. The experimental work investigated the evaporation rates of sessile droplets at reduced pressure using four different substrates with a wide range of thermal conductivities. Reducing the atmospheric pressure increases the diffusion coefficient of water vapour in the atmosphere and hence increases the evaporation rate. A mathematical model that takes into account the effect of the atmospheric pressure and the nature of the ambient gas on the diffusion of water vapour in the atmosphere was developed, and its predictions were found to be in encouraging agreement with the experimental results.

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