

Experimental investigation of the effect of thermal properties of the substrate in the wetting and evaporation of sessile drops

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Abstract

An experimental investigation on the evaporation of sessile drops is reported in this paper. The effect of thermal properties of the substrate is investigated by studying the evaporation of sessile drops on substrates with various thermal conductivities. The results show that the evaporation rate of drops is limited by thermal properties of the substrate especially for high evaporation rates. Furthermore the temperature of the evaporating drop is measured to show that it is dependent on both the evaporation rate and the thermal conductivity of the substrate. Preliminary results on the evaporation of water droplets under a reduced pressure environment show clearly that as evaporation is increased the gap between substrates having different thermal conductivities is widened. The results of this investigation demonstrate the crucial role played by the nature of the substrate in the process of spontaneous evaporation of sessile drops.

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1. Introduction

The topic of wetting and evaporation has been subject to an increasing interest by researchers in recent years. Ring stain formation, thin film coating and diseases diagnosis from biological fluids and DNA stretching in drops are few examples of exciting new applications where the understanding of wetting and evaporation of sessile drops is crucial. The extensive experimental investigations undertaken by various authors [1–7] gave insight in the physics of the wetting process during evaporation and the interaction between the two phenomena. Many of these investigations adopted the case of the spontaneous evaporation of liquid drops on substrates [1,4,8]. In these situations heat is brought from the ambient to allow the evaporation process to take place. Deegan et al. [1,7] investigated the evaporation of pinned sessile drops and the ring stain formation. Hu et al. [8,9] investigated the case where the droplet is small enough to be regarded as having a spherical cap shape and the contact line is pinned, the evaporation is considered mainly to be diffusion limited and can be regarded as quasi-steady-state process. In

the case of a droplet of water on a glass substrate, the model shows that at the initial contact angle of 40° the temperature increases from the top to the edge of the droplet, while at a contact angle of 10°, the temperature decreases. They suggest that this reversal of temperature-gradients direction occurs because at early times, the longer conduction path from the bottom of the glass to the top of the drop makes the temperature lower at the top than elsewhere, while at long times the faster rate at the edge makes it cooler there. Erbil and Dogan [10] investigated the cooling effect induced by the evaporation (self-cooling) of pendant drops. The main heat transfer mechanisms considered in this approach is heat conduction from ambient to the drop and latent heat of evaporation. The investigation attempted theoretically to evaluate the cooling effect due to evaporation for 11 liquids. The following expression for the mass evaporation rate was given:

$$\frac{dm}{dt} = 4\pi \frac{MDP_{v1}}{RT} r_1$$

where dm/dt is the evaporative mass flux, D the diffusion coefficient, r_1 the droplet radius, T the temperature, P_{v1} the vapour pressure near the interface, M the molecular weight and R is the gas constant.

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The interfacial temperature is derived from an energy balance giving:

$$T_S = T_{\text{air}} - \frac{M\lambda DP_{\text{vl}}}{RT_{\text{air}}k_f}$$

where λ is the latent heat of evaporation and k_f is the thermal conductivity.

According to this work a considerable surface cooling is observed especially for rapidly evaporating liquids, e.g. high P_{vl} values. They estimated a surface temperature difference to ambient of 20 °C for heptane evaporating into still air. Although the authors did not make measurements of interfacial temperature, they rely on experimental data reported in the literature where ΔT of 3 °C for *n*-butyl alcohol and 9 °C for toluene at 20 °C air temperature [13]. It is worth mentioning that most of the measurements available in the literature [13–15] are for pendant drops where the substrate does not play an important role. In fact conductivity through the holding fibre is usually neglected as in the work of Erbil and Dogan [10].

Kavehpour et al. [11] have reported the effect of thermocapillary stresses on the surface of an evaporating drop. Several materials have been used as substrates in these experiments and their thermophysical properties are found to have an important effect on Marangoni instability. The materials used are glass, brass and silicon. Experiments show that the amplitude and the critical onset thickness of the disturbances vary with the viscosity and the volatility of the liquid, and also with the surface roughness and thermal diffusivity of the substrate. The authors clearly show that while thermocapillary surface instabilities develop during spreading and evaporation of volatile drops on conductive substrates (silicon and brass), no surface oscillations were observed on glass substrate which is an insulator. The authors concluded that it is thus clear that heat transfer from the underlying substrate is very important in driving the onset of Marangoni instability in the fluid film.

Most of the investigations considered the spontaneous wetting and evaporation of sessile drops on various substrates. The evaporation mechanism is considered to be controlled by the diffusion of vapour into the ambient. To our knowledge the role of the thermal properties of the substrate has not been taken into account in any of these studies. Despite the fact that these thermal properties may be limiting in the evaporation process. Indeed the energy required for evaporation is drawn from the environment through various mechanisms. In the isolated drop case the cooling effect is determined by the evaporation rate. In the sessile drop case the cooling effect can also be linked to the thermal properties of the substrate.

The objective of this paper is to investigate the role of the substrate thermal properties in the evaporation process of sessile drops. In the first part of this paper the experimental setup is described, particular attention is given to dissociate the wettability influence and the thermal properties of the substrate. Different techniques to monitor the evaporation rates were implemented. In the second part the results are given, this concerns the investigation of four different substrates with various thermal conductivities. Preliminary results on varying the evap-

oration rate and its interaction with thermal properties of the substrate are briefly presented and discussed.

2. Experimental setup and procedure

The principal of the experiment consists of a drop of a controlled volume deposited on a substrate and allowed to evaporate spontaneously. The substrates used have dimension of 1 cm × 1 cm × 0.1 cm ($w \times l \times t$). Four different substrates were used chosen for their thermal properties: PTFE, macor, titanium and aluminium. All surfaces were coated with 3 µm aluminium layer. This will not affect the substrate thermal properties and gave all the four substrates the same surface energy, hence the same wettability by liquids. The surface roughness for all substrates was characterised using a ZYGO profilometer (microscope interferometer from ZYGO Ltd.). The 3D plot (Fig. 1) is the result of 3D interferogram which is transformed by frequency domain analysis. Indeed, an incoming light is split inside an interferometer, one beam going to an internal reference surface and the other to the surface to be analysed. After reflection, the beams recombine inside the interferometer, undergoing constructive and destructive interference and producing the light and dark fringe pattern. The results of the analysis indicated that all substrates have the same order of roughness, between 240 nm (PTFE) to 400 nm (titanium), Fig. 1.

All experiments were carried out in an environment where the temperature was controlled with an air conditioning unit with a precision of ±1 °C. Pressure and humidity were monitored to make sure that the experiments were performed in the same conditions. A DSA100 contact angle analyser from KRÜSS was used to measure the drop profile (angle, base and volume) (see Figs. 2–4).

An analytical balance (GR-2002 from AND) was used to measure the drop mass with a resolution of 0.01 mg. The measurements were computer controlled and the evolution of mass in time was obtained. In these experiments a CCD camera was used to obtain a top view of the drop. The recorded frames allow extracting the drop diameter, Fig. 5.

To measure the temperature profile inside and around the droplet, miniature thermocouple, size 0.25 mm (from Omega)

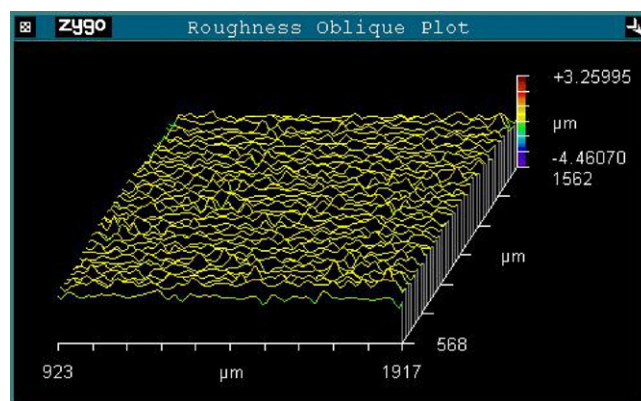


Fig. 1. Surface roughness profile (aluminium sample).

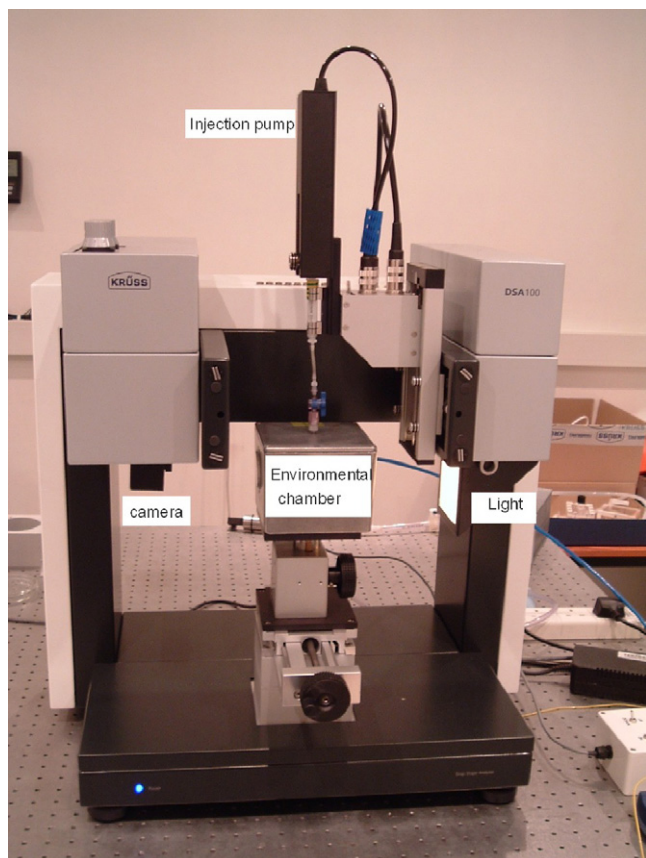


Fig. 2. DS100 contact angle analyser with a fitted environmental chamber.

is used. The response time of the thermocouple is 0.05 s and an accuracy of ± 0.01 °C, Figs. 6 and 7.

The liquids used for the experiments were pure deionised water, methanol and acetone. Using the DSA100 instrument droplets of initial volume ranging from 0.5 to 8 μl were deposited on the substrate. The drop evaporates and the various parameters were recorded in time. To ensure the reproducibility of the results a cleaning procedure of the substrates was

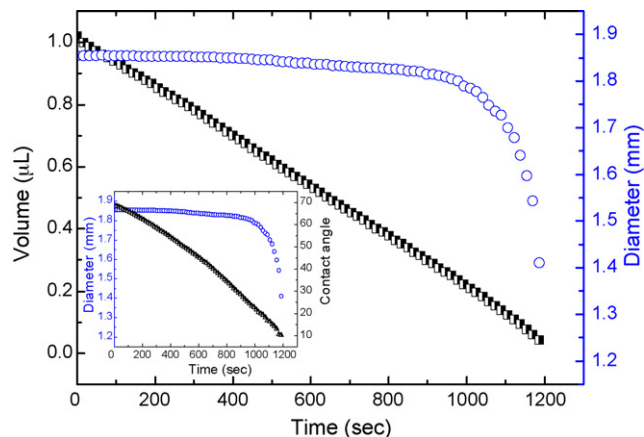


Fig. 4. Drop volume and base change in time (pinned drop, inset drop contact angle in time).

adopted. This includes an immersion in an acetone ultrasonic bath for 5 min then rinsing with deionised water and finally drying in an oven. The evaporation rates obtained using the DSA100 instrument and using the microbalance are found to be consistent for the drops used in the described conditions. A miniature thermocouple is used to measure the temperature in the gas phase as well as inside the drop at different locations (Fig. 6).

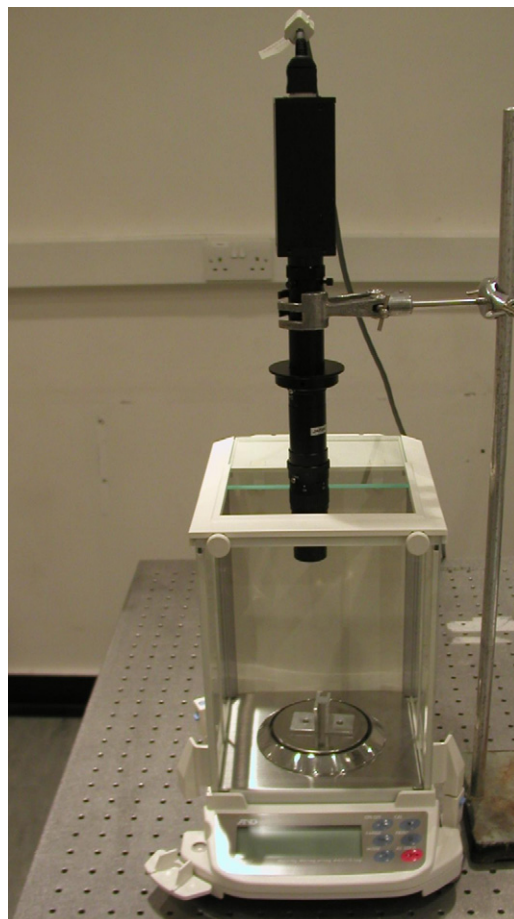


Fig. 5. Microbalance with a CCD camera mounted on top.

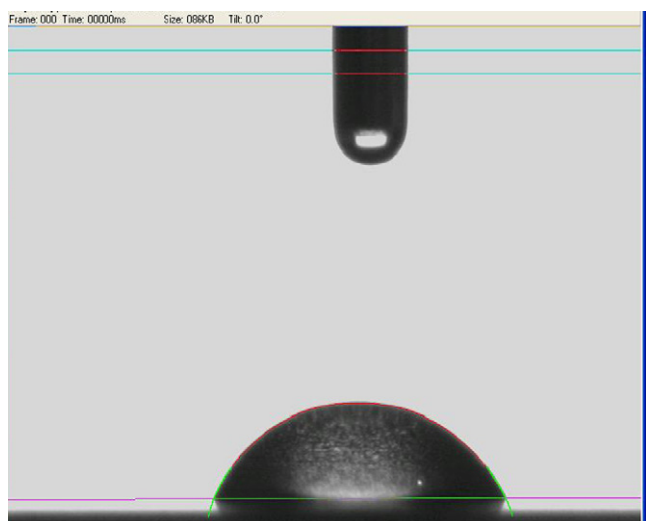


Fig. 3. Drop shape analysis.

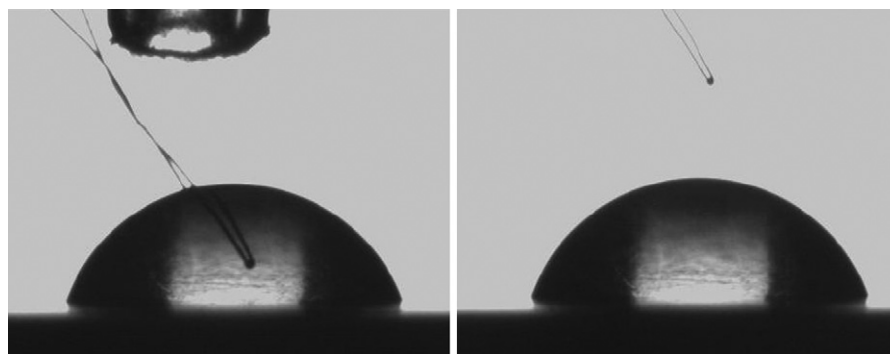


Fig. 6. Temperature measurement inside.

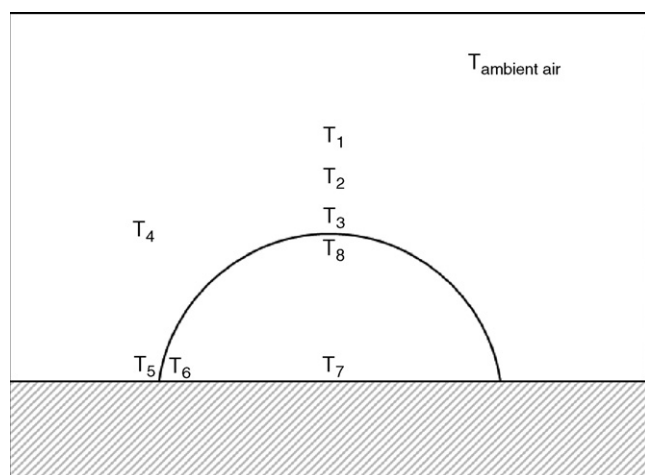


Fig. 7. A schematic of a liquid drop and outside the drop showing the locations where the temperature was recorded.

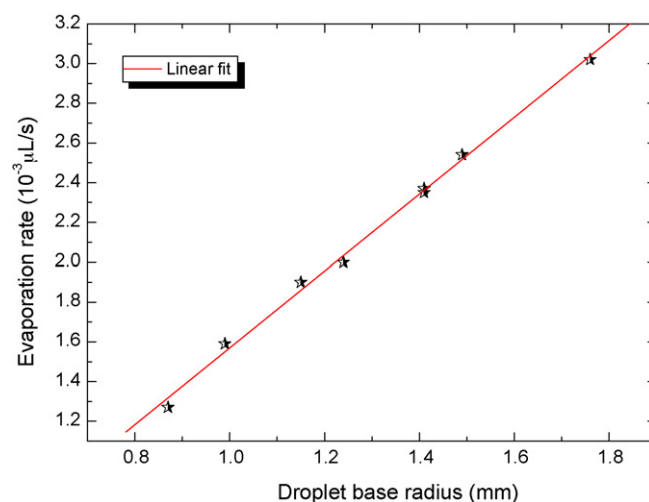


Fig. 8. Evaporation rate vs. drop base radius (linear trend).

3. Results

The evolution of the volume/mass of the drop with time was measured for pinned drops. It is found that on the aluminium coating (deposited on all substrates) the drop remains pinned in the first phase of evaporation. The drop volume decreases linearly with time. The evaporation rate is deduced from the slope of the linear fit of the data points. The results of this investigation confirm the conclusion about the trend in drop evaporation. The evaporation rate has a linear dependency on the droplet base radius (Deegan [1], Grandas et al. [12]), see Fig. 8.

Using the miniature thermocouple the temperature within the drop as well as in the environment is measured in two cases. In the first case the thermocouple is stuck on the substrate surface, the drop hanging from the delivery needle is then gently deposited on the substrate on the top of the thermocouple. The measured temperature in this case would be the ambient temperature before depositing the drop and the bulk temperature after

it is deposited. As can be seen in Fig. 9(b) after about 20 s the measured temperature drops at the very moment of drop deposition. The temperature is found to increase afterwards to slightly decrease and reach a steady state.

Temperature is also measured at different locations within the drop, the measurements revealed small temperature differences, however a systematic investigation is necessary to make definite conclusions (Table 1).

In the second the thermocouple is brought from the gaseous environment to the vicinity of the drop interface and dipped into the bulk liquid. The thermocouple in both situations (outside and inside the drop) is allowed to reach a steady state. This operation has been carried out for a number of times to confirm the results presented in Fig. 10 (Table 2).

The measured temperature is found to drop from the ambient temperature to a lower value corresponding to the drop bulk liquid. This temperature difference is used to describe the drop evaporation on the various substrates. The temperature

Table 1
An example of temperature measurement

	T1	T2	T3	T4	T5	T6	T7	T8	Tambient
PTFE	21.5	21	20.6	21.15	20.83	20.6	20.35	20.15	21.9
Al	21.5	21.25	21.1	21.42	21.44	21.34	21.4	20.95	21.8

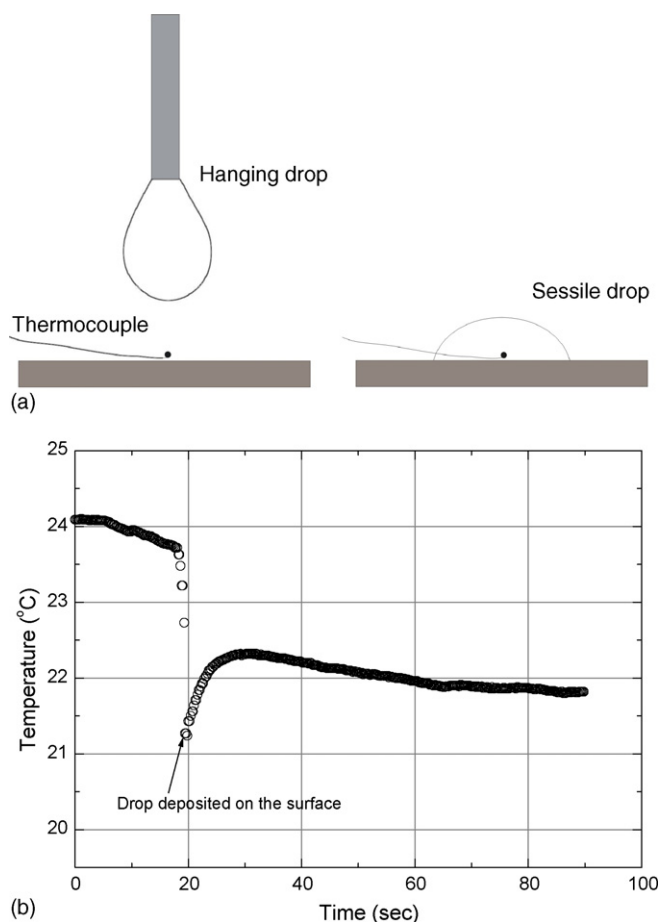


Fig. 9. (a) Drop deposition on substrate (thermocouple) and (b) temperature evolution as water drop is deposited on PTFE substrate on top of the thermocouple.

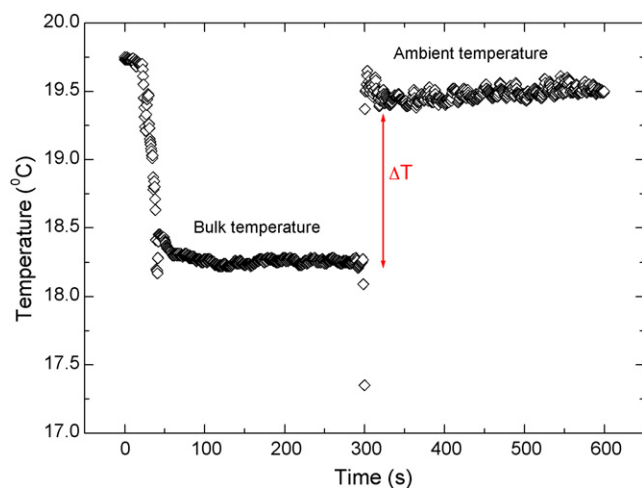


Fig. 10. Temperature measurement inside and outside the drop.

Table 2
Temperature difference between the ambient air and the droplet bulk, ΔT (K)

	Water	Methanol	Acetone
Al (237 W/m K)	0	3.6	4
Ti (22 W/m K)	0	–	–
Macor (1.5 W/m K)	0.6	–	–
PTFE (0.25 W/m K)	1.3	6.9	8.6

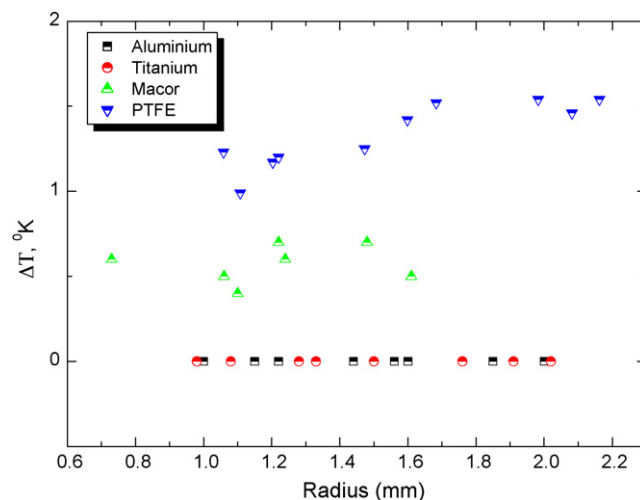


Fig. 11. Temperature difference ($T_{\text{amb}} - T_{\text{drop}}$) for water drops on various substrates.

difference as introduced above was measured for water drops of various sizes and on the four substrates. It is found that on both aluminium and titanium the temperature difference is negligible. It is however higher for macor and highest for PTFE, Fig. 11.

The evaporation rate is then plotted against drop base radius for the four substrates. Two important observations were made. The evaporation rate is found to be, respectively, higher for substrates with higher thermal conductivity. This difference is found to be more important for larger drops (greater evaporation rates). It is worth noticing however that there is virtually no difference whatsoever between aluminium and titanium despite an order of magnitude difference in thermal conductivity, Fig. 12.

In order to gain more insight into the investigated problem, various liquids were used on the two extreme substrates in terms of thermal conductivity (aluminium and PTFE). The liquids used have different thermophysical properties as well as wettability (see Table 3).

The evaporation rates of drops of various sizes made of the above liquids are measured on the two substrates (aluminium and PTFE). The results show that for each liquid the evaporation rate

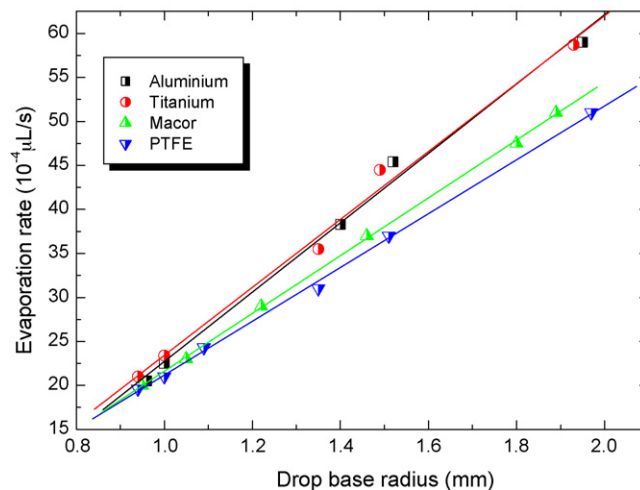


Fig. 12. Evaporation rate vs. drop base radius, water on various substrates.

Table 3
Liquids properties

	Methanol	Acetone	Water
Boiling point (°C)	64.7	56.3	100
Heat of vaporization (J/g)	1169	540	2444
Cp (J/g K)	2.53	2.15	4.18
Surface tension (mN/m)	22.07	23.2	72

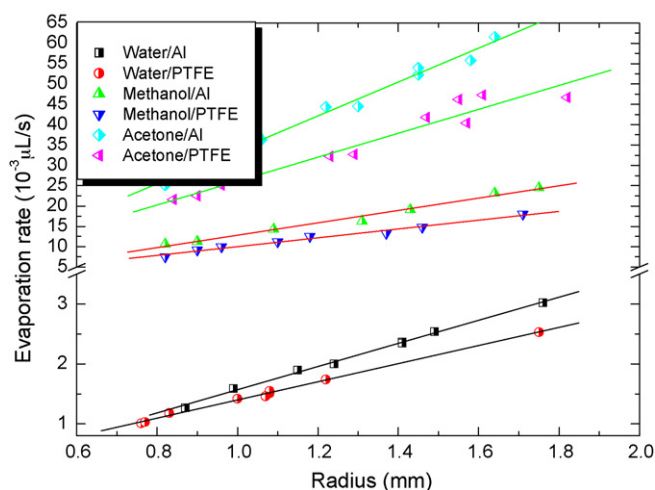


Fig. 13. Evaporation rates of various liquids drops on aluminium and PTFE substrates.

on aluminium is always higher than on PTFE. The difference in evaporation rates on the two substrates increases consistently with increasing the drops base radius, Fig. 13.

In order to investigate the role of evaporation kinetics and its interaction with the thermal properties of the substrate, experiments under reduce pressure environment were conducted. An environmental chamber where pressure is reduced from atmospheric to 100 mbar is used. The results of this investigation clearly shows that for the case of water drops evaporating on aluminium the evaporation rates are higher than on PTFE. The difference becomes more pronounced as pressure is reduced (see Fig. 14).

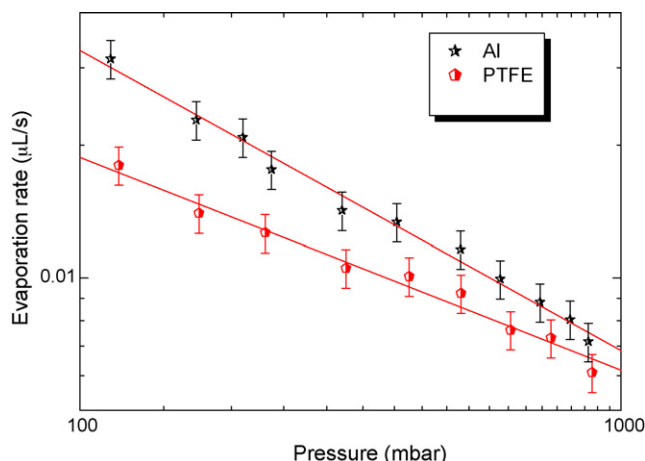


Fig. 14. Evaporation rates of water drops on aluminium and PTFE substrates.

4. Discussion

The evaporation of a drop in a gaseous phase is accompanied by a cooling effect. This latter being the results of the difference in energy consumed by the evaporation process (latent heat) and the energy supplied from the environment. The latter is brought by heat conduction and radiation from the ambient to the drop. This is almost equivalent to the case of a hanging drop when the thermal conductivity of the delivery fibre (needle) is neglected. This case has been demonstrated experimentally by many authors (Langstroth et al. [13], Ranz and Marshall [14] and Peiss [15]) and modelled by Erbil and Dogan [10].

When the drop is deposited on a substrate different situations can be encountered depending on the nature of the substrate and its interaction with the liquid. It is important to note that by depositing the drop a new interface is created (liquid–solid) and the evaporation interface (liquid–vapour) is also altered depending on the wettability of the liquid to the substrate. Two extreme cases can occur:

- A perfect thermal insulating substrate; in this case the evaporation rate will be modified according to the change of the liquid–vapour interface area. It is important to note that in this situation a cooling effect of the drop will be unavoidably observed due to the latent heat of evaporation.
- A perfect thermal conducting substrate, in this second case the evaporation rate is altered by two effects: the first is similar to the previous one (surface area change because of drop deposition) and the second mechanism which might be more important is the heat transfer between the substrate and the drop. The energy required for evaporation is brought in this case by conduction from the ambient (the gas phase) as well as heat conduction through the substrate. As a result, the evaporation rate is enhanced compared to the thermally isolating substrate. Following this simple analysis it can be deduced that the evaporation of a sessile drop is limited by the diffusion process of vapour in the gaseous phase in the perfectly thermal conducting substrate case.

An important difference between the hanging drop and a sessile one is that in the second case, the evaporation is non-uniform along the liquid–gas interface. For a sessile drop the evaporation is concentrated near the contact line, liquid–solid–gas (Deegan [1], Hu et al. [8]).

As a result, the evaporation is larger for drops with larger base radius following linear trend. This result has been deduced by many previous authors (Deegan [1], Grandas et al. [12]).

The temperature measurements performed when a drop is deposited on the substrate can be interpreted as follows: in hanging conditions the drop experiences important cooling effect, its temperature is below ambient air (this is the temperature corresponding in Figs. 9 and 15 to the initial temperature following the deposition of the drop, which is lower when the drop is longer hanged for a longer time, case of Fig. 9 compared to Fig. 15). As it is deposited on the substrate (this latter being at ambient

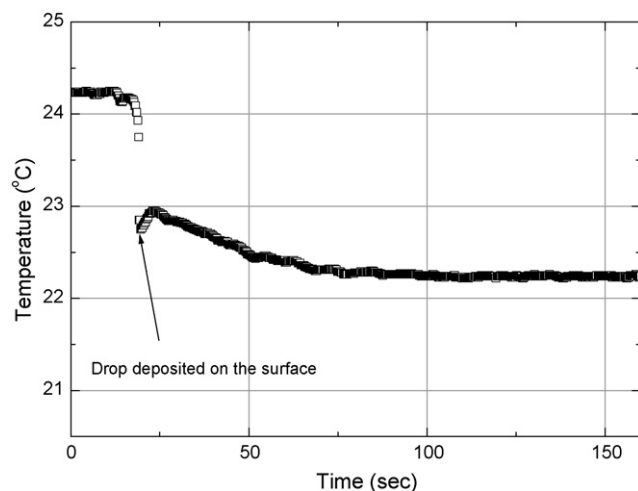


Fig. 15. Temperature evolution for a similar drop (Fig. 9) which has been hanging for a shorter period of time.

temperature) it will be heated by the energy conducted through the substrate from the ambient. This explains the rise in temperature after the drop touches the substrate. This temperature tends to a steady value that is below the ambient temperature in the case of thermally insulating substrate. This is resulting from an insufficient heat flux through the substrate to heat the drop up to the ambient temperature.

5. Conclusion

An experimental investigation of the evaporation of sessile drops deposited on substrate of various thermal properties has been undertaken. Some important conclusions can be drawn from this study:

- The evaporation rate of a sessile drop is influenced by the substrate thermal properties.

- The evaporating drop is found to experience an important cooling effect when the substrate is thermally insulating.

The increase of the evaporation rate is found to amplify the effects of the substrate thermal properties influence.

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