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Controlling arbitrary humidity without convection

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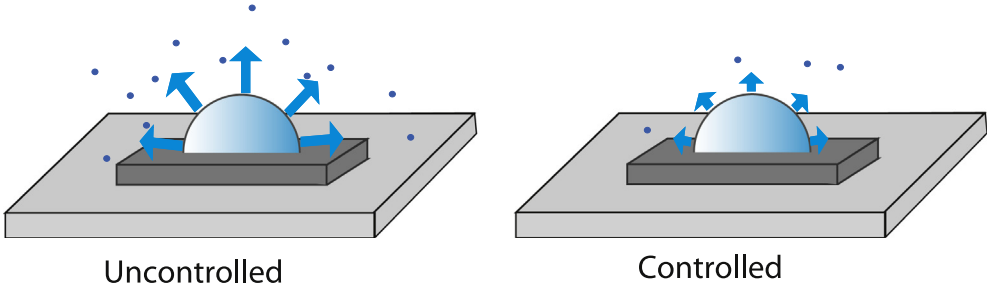
GRAPHICAL ABSTRACT



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ABSTRACT

In this paper we show a way that allows for the first time to induce arbitrary humidity of desired value for systems without convective flow. To enable this novelty we utilize a semi-closed environment in which evaporation is not completely suppressed. In this case, the evaporation rate is determined both by the outer (open) humidity and by the inner (semi-closed) geometry including the size/shape of the evaporating medium and the size/shape of the semi-closure. We show how such systems can be used to induce desired humidity conditions. We consider water droplet placed on a solid surface and study its evaporation when it is surrounded by other drops, hereon "satellite" drops and covered by a semi-closed hemisphere. The main drop's evaporation rate is proportional to its height, in agreement with theory. Surprisingly, however, the influence of the satellite drops on the main drop's evaporation suppression is not proportional to the sum of heights of the satellite drops. Instead, it shows proportionality close to the satellite drops' total surface area. The resultant humidity conditions in the semi-closed system can be effectively and accurately induced using different satellite drops combinations.

1. Introduction

Methods for arbitrary control of evaporation rate have many applications including drying [1,2]; cooling [3,4]; membrane separation [5]; thin-film deposition [6–8]; nano-composite films [9,10]; biomedical applications [11–13]; molecular biology [14]; food engineering [15,16]; geological science [17]; and materials [18], just to name a few. A number of methods have been introduced for this end, and as a rule they utilize either solutions of different salts [19], or, more commonly, saturated salt solutions [20–22] (the saturation maintains constant salt concentration in the solution and therefore produces constant humidity). There are various disadvantages to these methods: and the main one is the introduction of another chemical (the salt solution) which can contaminate the system [23,24] or corrode it or both. Other disadvantages include the need for different salt for each humidity, rendering a salt for a specific humidity potentially unavailable. Yet another problem with those methods is related to the actual practice of these systems: usually they are constructed in the lab, and the seal is reasonable but not perfect. To make sure that the desired humidity is maintained, typically air is bubbled through the salt solution,

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and carries with it the desired humidity to the actual system whose humidity we want to control and this flow overshadows any leakages that the system may have. The disadvantage is the need to create flow, and the added complexity of having a pump and an external big system to control humidity in a small system. As we shall see, in this paper we use basic principles of drop evaporations to overcome all these problems.

Drop evaporation has been studied extensively over the years [25–29] often in relation to different evaporation modes, most notably the so called CCR (constant contact radius) and CCA (constant contact angle) modes [30–32]. The existence of a CCR mode is related to pinning, which emanates from intermolecular re-orientation of the solid that is enhanced at the triple line as has been described experimentally and via simulation [31–33]. While exceptions to this rule exist [34], they will not affect the discussion of this paper.

Less attention, however, was given to evaporation suppression. Belman et al. [29] suggested that the evaporation rate near the triple line of high contact angle drops is suppressed by the vicinity of the solid. Indeed, Xu et al. [35] showed that the initial evaporation rate of a water droplet placed on a superhydrophobic surface is slowed down due to the large contact angle that results in a narrow wedge region of air along the contact boundary, where the liquid–vapor diffusion is restricted by the substrate. This results in an evaporation rate that is lower than predicted by Rowan model. In this paper we consider this understanding and choose a system in which the contact angle is close to 90° in which the Rowan model is expected to be more accurate. Such understandings help us approach the subject of this paper, namely utilizing drop evaporation to control relative humidity and suppress evaporation.

Open system (an imaginary control volume without real boundaries to the air) and closed system (a confined volume completely isolated from the open air) will induce no control or complete suppression respectively, while a semi-closed system can induce desired arbitrary control. At the same time, to be effectively used, such systems require better characterization. This paper aims to address this need. We show that this approach can induce arbitrary humidity in a simple and practical way that is advantageous compared to other evaporation suppressing methods [36,37]. We study experimentally the evaporation of a water drop surrounded by other water drops referred to as "satellite" drops when the entire assembly is in a semi-closed environment. The satellite drops are placed equidistant from the central drop in different configurations. We show that the central drops' evaporation rate is the same within the experimental error when surrounded by satellite drops of the same total liquid–vapor surface area even if their other parameters such as number of satellites, their heights or volume, differ (namely different configurations of the satellite drops). However, the central drop's evaporation rate is different if surrounded by satellite drops configurations whose total sum of heights are the same but their total sum of surface areas is different (seemingly contradicting theoretical evaporation rates). Similarly, the central drop's evaporation rate is different if surrounded by satellite drops configurations whose total sum of volumes are the same but their total sum of surface areas is different. The evaporation of all these drops proceeds with a constant contact radius (CCR) [25] mode during the time span presented in this paper except for drops placed in ambient air with no satellite drops in which case this mode is held only for the first 4 min.

In our group it has been reported that placing micro sized sessile water "satellite drops" around a central water drop produces effective evaporation suppression of the central drop [38,39], nevertheless, a detailed study on this effect is performed here for the first time.

1.1. Theory

Maxwell [40,41], showed theoretically that the evaporation rate ($\rho\frac{dV}{dt}$), namely the change of mass, ρV, with time, t, of a spherical liquid drop of density ρ and volume V suspended in air, follows Eq. (1):

$$\frac{dV}{dt} = -\frac{4\pi RDMP_o(1-RH)}{\rho R_g T} \tag{1}$$

where R is the liquid drop radius; D the liquid–vapor diffusion coefficient; M the molecular weight of liquid; P_o the saturated pressure of the liquid drop at its temperature T; RH the prevailing relative humidity and R_g the universal gas constant. For the case of a drop on a surface Eq. (1) was further modified by a few different theoretical studies (see nice summary by Erbil [30]). Of these, we use here the expression by Rowan et al. [42] as described in Eq. (2). The Rowan expression is accurate when the sessile liquid drop has a contact angle, θ, in the vicinity of 90°. This is close to our system when a drop is placed on a flat surface in ambient air [30,42–44]. The evaporation rate at relative humidity RH for this case is given by:

$$\frac{dV}{dt} = -\frac{2\pi hDMP_o(1-RH)}{\rho R_g T} \tag{2}$$

where h is the drop's height.

Our experiments were conducted under a hemispherical optical glass dome of R_D = 23 mm radius. Performing the integration over R_D in case of Rowan equation, instead of Rowan et al.'s open system, results in Eq. (3) below:

$$\frac{dV}{dt} = -\frac{2\pi hDMP_o(1-RH)}{\left(1-\frac{R}{R_D}\right)\rho R_g T} \tag{3}$$

where R is the radius of the sphere the drop is part of, R_D is the hemisphere (dome) radius, and h is the drop's height.

2. Experimental section

2.1. Materials

Silicon wafer were obtained from Virginia Semiconductor, VA (diameter: 76.2 ± 0.3 mm, orientation: ⟨1 1 0⟩ ± 0.9°, dopant: Boron, resistivity: 0.0034–0.0046 Ω cm, center thickness: 381 ± 25 μm) and cut into rectangular slides of 2 cm × 2 cm. Hydrogen peroxide (50 wt% in water) was obtained from Acros Organics. Ethanol (99.5%, 200 proof absolute), distilled water (0.1 μm filtered Molecular Biology Reagent), Ammonium Hydroxide (99.99%), Hydrochloric acid (37%), Toluene (99.5%) and Octadecyltrimethoxysilane (90% technical grade, CAS No. 3069-42-9) were obtained from Sigma Aldrich and used for self-assembly process [45].

2.2. Instruments

The UV Ozone Cleaner used was Procleaner™ from Bioforce Nanoscience. The oven used to bake the surfaces was Cole Parmer Model 5053-10. Humidity measurements were done with a hygrometer pen (Extech Instruments) from Cole Parmer. The goniometer used was from Wet Scientific. It includes: a hemispherical optical glass dome (internal radius and height of 23 mm with a thickness of 2 mm) fitting into a 1 mm deep 3 mm wide Teflon covered groove in the sample holder, and the related software for image processing from which geometric data (contact angle, height and diameter are measured) were obtained and verified manually.