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Evaporation of sessile drops under combined diffusion and natural convection

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ABSTRACT

Experiments were conducted to investigate the range of applicability of a commonly used assumption for evaporation models of sessile drops, that the transport mechanism that controls the evaporation is vapor diffusion. The evaporation rates of sessile drops of 3-methylpentane, hexane, cyclohexane, and heptane were measured. The radius of the drop contact line was constant during the measurements and drops of radius from 1 mm to 22 mm were studied. It was found that a diffusion-controlled evaporation model underpredicts the evaporation rate from 36% to 80% depending on the drop size. The increase in the evaporation rate was attributed to a second transport mechanism, natural convection of the vapors, and an empirical model was developed for conditions of combined diffusive and convective transport. Over the broad range of volatilities and drop sizes studied, the evaporation rates computed using the combined transport model agree with the measured values with less than 6% root mean square error.

1. Introduction

The evaporation of sessile drops on solid substrates continues to be the subject of ongoing research not only due to its intrinsic scientific value but also because evaporation plays an important role in many practical applications, e.g. coating, painting and printing. Modeling the dynamics of a sessile drop as the drop first expands to wet the surface and then recedes due to the loss of volume from evaporation has been accomplished recently with very good qualitative agreement between the model and measurements of drop contact line radius and contact angle [1–7]. Good success has also been achieved in modeling the dynamics of a sessile drop which is pinned to a flat horizontal substrate [8–11]. In the case of a pinned drop, the radius of the contact line remains constant until sufficient volume is lost due to evaporation to cause the contact line to pull from its original position as the contact area of the drop reduces. Models for both wetting and pinned drops assume that the evaporation is quasi-steady and the rate is controlled by the rate that vapor diffuses away from the liquid surface. The purpose of this study is to investigate the applicability of the diffusion-controlled evaporation assumption for sessile drops and to develop an empirical evaporation model for conditions in which both diffusion and natural convection are important.

As discussed by many authors, the problem of quasi-steady, diffusion-limited evaporation of a drop is governed by the steady Laplace equation. As reported by Thomas and Ferguson in 1917, Stefan was the first to obtain a solution for the evaporation of a flat, circular surface and to demonstrate that the evaporation rate was proportional to the radius of the surface, and not the area [12]. Stefan's solution was obtained by analogy to the electrostatic case of a charged conductor. Using a similar electrostatic analogy, expressions have been derived for the evaporation rate of a sessile drop for two cases, one in which the contact angle remains constant and the contact area reduces, and the second case in which the contact area remains constant, i.e. a pinned drop, and the contact angle reduces [8,11,13,14]. For both of these cases, the rate of evaporation was found to be proportional to the radius of the contact line, in agreement with Stefan's result. According to these solutions, the local evaporative flux is low but increases gradually moving from the center of the drop toward the contact line. The flux becomes large in the region of the contact line and, in fact, one of the practical difficulties of these analytical solutions is that the flux becomes infinite along the contact line.

Despite the fact the flux becomes infinite at the contact line, the flux may be integrated over the surface of the drop to compute the overall evaporation rate. Other approaches that have been taken to model the evaporation of sessile drops are to use a smoothing function or a separate evaporation model in the region of the contact line [2–8,11,14], or to use an empirically derived constant of proportionality to relate the total evaporation rate to the transient radius of the drop contact line [1,3,15]. Researchers also have worked to improve the expression for the evaporation rate of sessile drops by accounting for effects such as evaporative cooling [11,15] and parabolic surfaces [11].

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While the direct proportionality between the total evaporation rate and the contact line radius has been experimentally validated for both wetting and pinned sessile drops undergoing diffusion-controlled evaporation, in the words of Starov and Sefiane, 'its demonstration from the theoretical point of view as well as the physical phenomenon behind it remain unclear' [15].

It should be noted that the vast majority of the experimental validations of the quasi-steady, diffusion-controlled evaporation model have been accomplished with drops having a radius less than 3 mm. However, Poulard et al. compared the results of experiments with sessile drops having a radius of up to 8 mm with those of smaller drops and reported a modest difference in the behavior of the transient drop radius as a function of drop size [6]. They concluded that the sensitivity of their solution to the capillary number, which contains an evaporation rate parameter, needs to be 'smoothed out'. A much longer time ago, Thomas and Ferguson measured the evaporation rates of water contained in circular pans of radius from 21 to 100 mm and determined that on average the evaporation rate varied with the radius raised to the power of 1.69 [12]. For those experiments, the liquid surface was 7 mm below the rim of the pan, and so the water in their experiments cannot be considered sessile drops. Still, their results call into question the applicability of a diffusion-controlled model for the evaporation of large drops. In the same paper, the authors report that as the depth of the liquid surface from the rim of the pan increases, the dependence of the evaporation rate approaches the square of the radius, which is expected for one-dimensional diffusion.

It is interesting to consider what the range of applicability of the quasi-steady, diffusion-controlled evaporation model is. Contrary to the results derived from the solution to the steady Laplace equation, the evaporative flux along the contact line is finite. Therefore, as the radius of the contact line increases, the ratio of the drop surface area to the contact line length increases, and consequently it is reasonable to expect that at some point the evaporation rate would become proportional to the drop radius raised to a power greater than 1. For very large radii, the evaporation rate may be expected to become proportional to the square of the radius (area). Furthermore, it is interesting to consider how the vapor density above the drop may limit the applicability of the diffusion-controlled evaporation assumption. For a vapor density that is either very low or very high in comparison to the ambient gas density, one would expect natural convection to influence the rate of vapor transport from the drop surface and thereby affect the evaporation rate.

In a previous study, schlieren imaging was used to view the vapor clouds that formed over pinned hydrocarbon drops of radius 6.5 mm [16]. The schlieren videos show the vapor clouds flowing over the surface of the drops indicating the occurrence of natural convection. Further, by modifying the geometry of the substrate surrounding the drop, the relative influences of diffusion and convection were adjusted. That study demonstrated the potential for natural convection to increase the evaporation rate compared to diffusion-limited evaporation. However, drop size was not varied and so the relationship between evaporation rate and drop radius was not determined.

The influences of drop size and vapor density on the evaporation rate are the subjects of this study. The goal is to better define the range of applicability of the diffusion-controlled evaporation model and to provide insight into the evaporation process for cases in which natural convection may be significant.

2. Materials and methods

The evaporation rates of pinned, sessile drops in an initially quiescent atmosphere were measured for a wide range of drop sizes. The ambient temperature and pressure were $23.2 \pm 0.7\,^{\circ}\mathrm{C}$ and 1 atm. Four hydrocarbon components were used: 3-methylpentane (3MP), hexane, cyclohexane, and heptane. 3MP and hexane are geometrical isomers and cyclohexane approximately is a third isomer. These isomers have nearly equal molar masses and heats of vaporization but significantly different equilibrium vapor pressures. Heptane was included in the study in order to expand the range of volatilities so that the equilibrium vapor pressures vary by a factor of four. Natural convection is driven by a density difference, and the difference in densities of the vapor–air mixture at the surface of the drop, ρ_m (assuming a saturated mixture) and the surrounding air, ρ_a, i.e. $(\rho_m - \rho_a)$ varies by a factor of three for the components in this study.

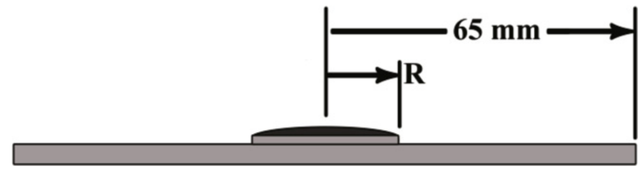

Fig. 1. Section view of the substrate and drop, shown in profile. The drop, shown in black, is pinned to the edge of the circular platform that is raised slightly above the surface of the circular base.

The drops were created in a manner similar to what is reported in Ref. [16]. To create drops of a specified size, a pipettor or syringe was used to deposit a controlled amount of liquid on a flat circular platform that is raised slightly above the base horizontal surface, as shown in profile in Fig. 1. In this figure, the black area represents the drop. The platform is raised above the base surface in order to create a sharp circular edge to which the liquid attaches and thereby determines the size of the drop. As the drop evaporates, the contact area remains constant until eventually the drop volume is insufficient to cover the surface of the platform and the drop pulls free from the edge. All of the measurements were conducted prior to the time at which the drop pulls from the edge. In this manner, the drop radius, R, was varied from 1 to 22 mm while the radius of the base horizontal surface remained constant at 65 mm. (Note that for large radii, the term 'film' may be more appropriate than 'drop' but for consistency we use the term drop regardless of the radius.)

Initially, all of the platforms were 1 mm above the base surface. The platforms with a radius of 4 mm and smaller were lowered to 1/2 mm above the base due to a concern that a geometry with a small aspect ratio of radius to elevation would influence the evaporation rate. However, the measured evaporation rates were equal for the two elevations. The platform and base are composed of a single piece of aluminum to avoid problems of poor thermal contact between the platform and base.

To prevent ambient drafts from influencing the measurements and to ensure an initially quiescent atmosphere, all experiments were contained in an enclosed volume (ca. 6200 cm^3). Small vents were located at the base of the enclosure to allow vapor, which is heavier than air, to escape and thereby prevent it from accumulating. A comparison of measurements conducted with and without the vents indicated that the evaporation rates of large drops were moderately lower without the vents in the enclosure. Further investigation indicated that the reduction in the evaporation rate was due to the vapor collecting and partially filling the enclosure. For drops having a radius of 8 mm and smaller, no difference in the measured evaporation rates was measured with and without the vents.

Evaporation rates were measured by a simple gravimetric technique, using an analytical balance having a resolution of 0.1 mg. The balance was connected to a computer using the RS232 interface and mass data were collected at a rate of 10 Hz. As shown in Fig. 2, the mass reduces at a constant rate, which is typical of all