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Condensation of a non-wetting fluid on a solid surface

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Abstract

Theoretical studies of a drop moving under condensation from the surrounding vapor, have been provided. Two cases are considered. In the first, the rate of condensation is large that the drop "moves" because condensation has changed its dimensions. The model provided here shows that the rate of spreading is a constant, proportional to the heat flux and inversely proportional to the macroscopic contact angle. This compares well with available experimental data. The other model where the rate of condensation is small, is taken from existing results and comes close to explaining one set of experimental data. It is based on the use of viscous forces as the primary rate mechanism. Its shortcomings have been discussed.

Keywords: Condensation; Thin liquid films; Spreading rate

1. Introduction

Evaporation from wedges, drops and thin films have received considerable attention, in both experimental and theoretical considerations [1–6]. Where thin liquid film exists, disjoining pressure is used. It arises as a body force in the equations of motion [7] along with the capillarity. It also arises in changes that affect the chemical potentials. In turn, it affects boiling points and saturated vapor pressure [8] and which in turn it affects the rate of evaporation [9]. Of course, the capillary forces need to be considered alongside as well.

It also appears that condensation is exactly the opposite of the evaporation process although some care must be used before such assertions can be made. Two recent cases of condensation studied by Wayner and co-workers [10,11] appear very interesting where the liquids are non-wetting. Condensation happens on a cold surface where a thin film is first formed. Then drops nucleate and grow/spread over the thin films. The film thickness remains constant and the investigators measure the kinetics of the drop growth/spreading. The disjoining pressure that gives rise to such a behavior is shown schematically in Fig. 1. They were first measured by Derjaguin and Zorin [12], where the dashed curve cannot be measured, but now a sound theory exists for it [13]. The disjoining pressure Π is related to the unsaturation in the vapor pressure, and falls to zero as the vapor pressure reaches the saturation value. As the vapor pressure is increased, the film thickness h also increases. But at point P, the thin film of thickness h_P is in equilibrium with an infinitely thick film, that is, the bulk liquid. Hence as we move to the right of the point P, droplets appear.

A short description of a model for evaporation/condensation is also described here in brief. A model to describe the wetting kinetics has been given by de Gennes [14]. The viscous dissipation in a wedge is equated to the rate of surface work done. One important assumption here is that the lubrication theory approximation holds in the wedge shown in Fig. 2. It assumes that the flow rates and the slope of the wedge are small. Quasistatic approximation is made, it is also assumed that only the tangential velocity v_x is significant and it varies mainly in the z-direction. Ybarra and Neogi [6] included in the dissipation the heat transfer terms and the results compared well with the available experimental data. However, as they retained the lubrication theory approximation, their solution is valid at low rates of evaporation/condensation as they point out. Consider the condensation shown with an arrow in Fig. 2. If the rate of condensation is high, then the normal velocity v_y can no longer be ignored and the lubrication theory fails. For this particu-

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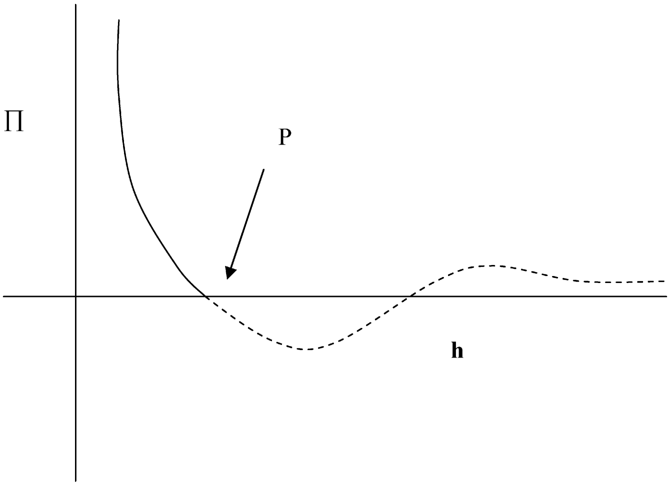

Fig. 1. Disjoining pressure as a function of film height. The dashed line represents regions that cannot be determined using experiments. The point P where $\Pi_{\mathrm{P}} = 0$, gives us the thickness of the film h_{P} which would be in equilibrium with a liquid drop.

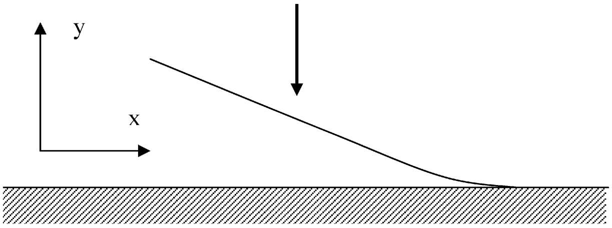

Fig. 2. Shape of the wedge that is usually analyzed under lubrication theory approximation. The bold arrow downwards represents condensation. If condensation is significant, v_y will appear and the lubrication theory will not work.

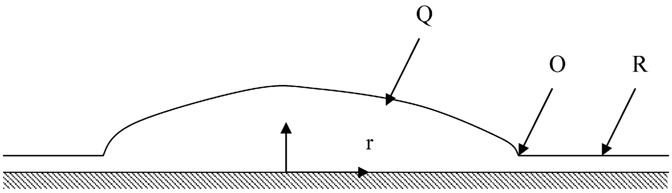

Fig. 3. The shape of a drop ending in a thin film and growing with condensation is shown schematically. Point R is where the thin film remains at constant thickness. Point O is the moving contact line. Point Q is where the film is sufficiently thick that the disjoining pressure is zero.

lar case where the rate of condensation is high that the drop "moves" because of its growth, there are no theoretical results available.

Below, a model for high condensation rates is first made available. It is shown that it satisfies the 2-propanol data [11]. In a shorter section, it is shown that the n-butanol data [10] are close but not equivalent to the small condensation rate data. In these experiments, condensation leads to a thin film and then droplets form and grow/spread. Various quantities associated with the growing/spreading droplets are measured. One key observation was that the thickness of the thin film ahead of the drop (region R in Fig. 3) did not change with time. Whereas the vapor was maintained at constant temperature T_{s} and at a pressure, which is assumed here to be supersaturated p_{ss}, that is above saturation pressure p_{s}, the substrate was cold at T_{w} as heat was withdrawn from it. The investigators conclude from indirect evidence that the heat flux was a constant in an experimental run.

They also found that although the microscopic contact angle in these cases were zero, there was a macroscopic contact angle α in the thicker part of the drop which remained a constant although the dimensions of the drop were changing with time. This angle appeared to correspond more with the slope of the basic shape of the drop (segment of a sphere) extrapolated to the horizontal and were located at a point where the slope was the highest.

2. High condensation rates

It is assumed here that the rate of condensation is high such that the drop "moves" because of the change in shape. If viscous flow is ignored, the film thickness $h(r)$, shown in Fig. 3, is governed by the augmented Young–Laplace equation

$$-\gamma\left[\frac{\partial^2 h}{\partial r^2} + \frac{1}{r}\frac{\partial h}{\partial r}\right] - \Pi = p_{\mathrm{c}}, \tag{1}$$

where γ is the surface tension, p_{c} is the capillary pressure and a constant. The term in the square brackets is the curvature where it is assumed that the slopes are small. At point R, there is no curvature and

$$-\Pi_{\mathrm{R}} = p_{\mathrm{c}}. \tag{2}$$

In the drop, that is, at Q,

$$-\gamma\left[\frac{\partial^2 h}{\partial r^2} + \frac{1}{r}\frac{\partial h}{\partial r}\right] = p_{\mathrm{c}}. \tag{3}$$

Since the film thickness is high there, the disjoining pressure is negligible. It also shows that the curvature is a constant there and Eq. (3) can also be written as

$$\frac{2\gamma}{R} = p_{\mathrm{c}}, \tag{4}$$

where R is the radius of curvature of the profile given by a segment of sphere. It shows that p_{c} is positive. Hence, from Eq. (2), Π_{R} is negative. The only way this is possible from Fig. 1 is if the thickness at R lies to the right of point of P. That is, the thickness at R in Fig. 3 is a non-equilibrium thickness.

Thermodynamics is considered next. The changes in chemical potential due to changes in pressure and temperature are given by

$$\mathrm{d}\mu_{\mathrm{l}} = v_{\mathrm{l}}\,\mathrm{d}p_{\mathrm{l}} - s_{\mathrm{l}}\,\mathrm{d}T = v_{\mathrm{l}}\,\mathrm{d}(2\gamma/R - \Pi) - s_{\mathrm{l}}\,\mathrm{d}T, \tag{5}$$

where μ is the chemical potential, v is the specific volume, p the pressure and s the specific entropy. The subscript l stands for the liquid and the excess pressure in the liquid (over the saturation vapor pressure) has been used following the results from Eqs. (1)–(4). In the vapor phase

$$d\mu_{\mathrm{v}} = v_{\mathrm{v}}\,\mathrm{d}(p_{\mathrm{ss}} - p_{\mathrm{s}}) - s_{\mathrm{v}}\,\mathrm{d}T, \tag{6}$$

where it has been assumed that the pressure in the vapor phase remains constant at the saturation pressure. Subtracting Eq. (5)