RESEARCH ARTICLE | MAY 15 1991

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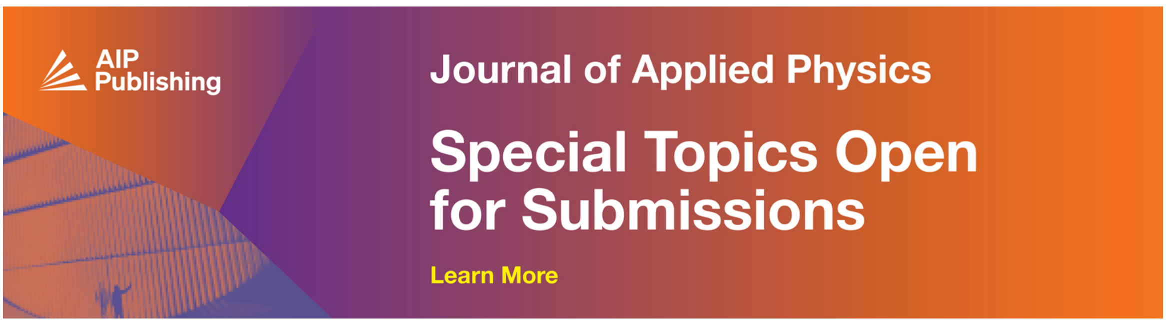
J. Appl. Phys. 69, 7034–7036 (1991)
https://doi.org/10.1063/1.347643



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Evaporation of small drops

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(Received 27 December 1989; accepted for publication 22 January 1991)

A theoretical approach to the phenomena of small drop evaporation is presented here. By considering the momentum balance and the energy balance surface equations, it is found that the evaporated mass rate is a parabolic function of the drop's radius. This theory also predicts that the evaporation proceeds until the drop radius gets equal to the "Tolman's length." At this limit the liquid and the vapor become indistinguishable phases. The results are compared and discussed at the light of recent experimental work.

I. INTRODUCTION

Under certain thermodynamic conditions a liquid drop in equilibrium with its own vapor can start to lose mass and to transform itself into vapor. This process of mass transfer across the interface, called evaporation, may happen rapidly or gradually. In the first case an instability is produced because of the marked increase in the evaporation flux of the surface. This happens when the vapor of a liquid-vapor system is pumped out gradually.[1] The mechanism of this instability has been studied early,[2] but the most familiar example is the slow evaporation. Such a motion is a phase transformation, where gradually, gently, and continuously the droplet loses mass and diminishes in size. The continuous mass transfer and decreases in the volume of the drop produces an increase in the vapor phase at the expense of the liquid phase.

Some theoretical and experimental aspects of this kinetic mass transfer phenomena can be found in recent works. Numerical results for the evaporation of a spherical particle show the behavior of the lines of current.[3] An experimental study of the evaporation of a small drop maintained at constant volume shows,[4] contrary to the earlier theories[5] and experiments,[6] that the evaporation rate is a parabolic function of the drop radius instead of being proportional to the radius.

We will describe the evaporation process by using surface thermodynamic equations. The results will be cautiously compared with the mentioned experiment.

II. HYDRODYNAMICS OF A LEVITATING DROP

As far as we try to explain the evaporation of a spherical drop, we must recognize and examine the natural connection between the interface and both substrates, the internal liquid phase (L) and the external gas phase (G). Let us assume for the sake of simplicity that the tangential component of the velocity at the drop surface is null and that we deal with a flow in which the interface is reduced while retaining its spherical shape. The dynamical connection between the surface and its surroundings is given by the following momentum balance equation. In the radial direction it reads:[7]

$$V_r^s \partial\Gamma/\partial t + (p^L - p^G) + (p_d^L - p_d^G) = 2\sigma_0/r - 2\sigma_0\delta/r^2 + (4\bar{K}/r^2)V_r^S \quad (1)$$

where V_r^S is the radial velocity on the drop surface, $\Gamma = \int\rho(r)dr$ is the mass per unit surface. $\mathbf{P}^L$ and $\mathbf{P}^G$ are the static liquid and gas pressure, respectively. In the following we will drop $\mathbf{P}^G$ because $\mathbf{P}^L$ is usually much larger than $\mathbf{P}^G$. Equation (1) reduces to the generalized LaPlace equation[8] if all the dynamic terms are neglected. $\mathbf{P}_d^L - \mathbf{P}_d^G$ is the dynamic pressure exerted on the liquid surface[9] ($\mathbf{P}_d = \rho V_r^2$); only exists in the direction parallel to the fluid velocity. σ_0 is the surface tension of a planar surface, δ the "Tolman's length"[8] of the order of the interfacial width. $\bar{K}$ is the coefficient of dilatational surface viscosity and r is the drop radius.

From Eq. (1) the surface mass rate flow is:

$$\partial m/\partial t = 4\pi[4\bar{K} - 2\sigma_0\delta/V_r] + [8\pi\sigma_0/V_r]r + [4\pi(p_d^G - p^L)1/V_r]r^2 \quad (2)$$

where we have taken into account the above-mentioned assumptions. The radial velocity just outside and at the drop surface are considered to be the same and they will be indicated by V_r.

Equation (2) links surface and bulk properties; if the radial velocity is constant the evaporative rate of a spherical drop is a parabolic function of the radius.

The thermal balance equation[10] in the stationary case is

$$[\rho V_r h]_G^L = [K\partial T/\partial r]_G^L. \quad (3)$$

where h is the specific enthalpy (enthalpy per unit mass), K is the heat conductivity, and $[\,]_G^L$ indicates the difference between the liquid and gas properties. Within the drop the liquid velocity is null, that is there is only conduction, then from Eq. (3) the gas velocity is

$$V_r = K_L(\partial T/\partial r)_L/\rho_G h^G \quad (4)$$

we have disregarded $K_G(\partial T/\partial r)_G$ because $K_G < K_L$, where $(\partial T/\partial r)_L$ indicates the radial thermal gradient of the liquid drop, K_L represents the conductivity, while h^G is the enthalpy density of the gas. It must be kept in mind that evaporation cools the water layers below the interface.[11] That is, between the interior and the drop surface there will be a constant temperature difference, which ends when the evaporation process comes to an end. It could be assumed that the

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drop temperature increases proportionally to the radius.[12]

Finally, by substitution of Eq. (4) into Eq. (2) the evaporation mass rate is:

$$\partial m/\partial t = a_1 + a_2 r + a_3 r^2 \qquad (5)$$

where

$$a_1 = 4\pi\left[4\overline{K} - \frac{2\sigma_0 \delta \rho_G h^G}{K_L (\partial T/\partial r)_L}\right],$$

$$a_2 = \frac{8\pi \rho_G \sigma_0 h^G}{K_L (\partial T/\partial r)_L},$$

$$a_3 = \frac{4\pi \rho_G h^G (p_d^G - p^L)}{K_L (\partial T/\partial r)_L}.$$

Equation (5) resembles that found experimentally by Peiss where the evaporative mass rate is a parabolic function of the drop radius. In the limit of null mass evaporation rate Eq. (5) predicts the following drop radius

$$r_c = r_{(\partial m/\partial t) = 0} = \delta. \qquad (6)$$

This equation tells us that a drop will evaporate until it reaches a critical radius proportional to the "Tolman length." This length[13] is of the order of a few molecular diameters far from the critical point. At this limit there is no difference between the liquid and the gas phase.

III. COMPARISON WITH THE EXPERIMENT

Before comparing our results with the curve fitting equation predicted by Peiss, let us describe succinctly the experiment. A water drop, formed on the blunt end hypodermic needle within a closed chamber, was maintained at constant volume by injecting water into the drop through the hypodermic needle at the same rate at which the evaporation evolves. The evaporative mass rate measured[4] in this way over a wide range of drop diameters in CGS units (Gaussian system) reads as:

$$\partial m/\partial t = 4.51\times 10^{-4} + 3.975\times 10^{-2} r + 2.29\times 10^{-1} r^2. \qquad (7)$$

In order to compare this equation with Eq. (5), we will evaluate each of the coefficients of the later equation as follows. The air density is not specified in the experiment; we estimate it by using the ideal gas equation. We assume that the air pressure is around 1 Torr, then the corresponding air density is $\rho_G = 14.8\times 10^{-7}$ g/cm^3. If the thermal gradient is $\Delta T/\Delta r = 10^{-1}$ °C/cm, the conductivity[9] $K = 1.44\times 10^{-3}$ cal/s cm °C and the specific enthalpy[15] is $h^G = 10.866$ cal/mol. The corresponding velocity evaluated from Eq. (4) is $V_r = 3.24\times 10^4$ cm/s, while the "experimental" value coming from Eq. (7), with σ_0(water) $= 73$ dyne/cm is V_r exp $= 4.61\times 10^4$ cm/s, the drop surface fluid moves with velocities of the order of the free particle velocity.

The theoretical coefficient corresponding to the linear term evaluated under all the above assumptions is $a_2 = 8\pi\sigma/V_r = 5.66\times 10^{-2}$ g/s cm while the experimental is 3.975×10^{-2} g/s cm.

Let us have a look at the coefficient a_3. The positive part is associated with the dynamic pressure and is equal to 6.02×10^{-1} g/s cm^2, while the negative part is much smaller because the internal static liquid pressure is less than the dynamic gas pressure $\mathbf{P}_L < \mathbf{P}_d^G$, otherwise the drop will grow instead of being evaporated, then the coefficient a_3 will be of the same order of magnitude as the experimental. Finally, we examine the independent term a_1. It has two parts, one related to the drop surface viscosity, the other to the Tolman length. Experiments on the propagation of capillary waves on plane liquid surfaces have suggested[16] that water surface viscosity is around $1.2\times 10^{-5} sp$ surface poise $=$ g/s). There is no definite opinion if pure plane liquid-vapor surfaces have surface viscosity. In the case of a curved surface (e.g., a drop) the question is worst because little is known about it.[17] Then we are not able to predict the positive contribution to a_1, but if it would exist it should be of the order or less than the negative contribution to a_1 (we will come back to this point below). This negative contribution is 4.245×10^{-9} g/s, where the water molecular diameter was considered to be around 2.5 Å.[18]

IV. COMMENTS ON THE THEORY AND THE EXPERIMENT

Many problems have recently been understood and explained on the basis of the surface balance equations. Microscopic,[19] three-dimensional,[4,20] and bi-dimensional[1,21] approaches, have been permitted to obtain momentum and energy surface balance equations. Equation (1) is a momentum surface balance equation in spherical symmetry. The radial direction here has been considered of central importance in the explanation of the evaporation process. At equilibrium this equation reduces to the Laplace formulas $\Delta p = 2\sigma/r$. It has been included in this equation the effect of curvature dependence of surface tension[8] $[\sigma = \sigma_0(1-\sigma/r)]$. Since Tolman, many theoretical and experimental works have been done on the subject of curvature dependence of surface tension and all works agree that there is a decrease of surface tension when reducing the droplet radius.[22] We have also included in Eq. (1) the dissipative effect of surface dilatational viscosity. It must be mentioned that in contaminated liquid surfaces or with certain monolayers the evaporation rate is reduced.[6] Surface viscosity values of a plane liquid-vapor interface having a clean surface remain an open question. No investigations have been done on this problem on droplets. According to the present model of evaporation, surface viscosity of pure liquids could be zero or $\overline{K} \lessdot \sigma_0 \delta \rho_G h^G / 2K_L (\partial T/\partial r)_L$, that is of the order or less than the negative contribution to a_1, otherwise it will be predicted by Eq. (5) a positive mass flux for a negative drop radius. The other two terms a_2 and a_3 are related to the driving forces.

I will comment on some aspects of the experiment done by Peiss. By examining Eq. (7) we see that a_1 exp $= 4.51\times 10^{-4}$. The positive character of this quantity implies a positive mass flux for a negative drop radius. Under these circumstances, the following remarks on the experiment will be of some help. First, the droplet was formed on a blunt-end hypodermic needle. Second, the surface temperature of the drop was measured with a thermocouple having a junction diameter of 0.075 mm. Third, the glass capillary microelectrode may have an effect upon the drop. All these facts indicate that we are not dealing with an isolated droplet but with a droplet in contact with many and different sharp surfaces. Here spreading and wetting will spontaneously appear, modifying the shape of the drop. The precursor film will wet the surface close to the drop and will also be reduced by evaporation. This constant evaporative mass quantity as well as the wetting liquid mass, must be subtracted from the total mass if we want to deal with the evaporation of a spherical drop. I believe that the systematic loss of mass by evaporation and formation of the wedge-precursor system, could be responsible for the positive character of a_1 in Eq. (7). In this sense one must be cautious in comparing theory and experiment. Beside this difference the present theoretical analysis for a free or levitating drop predicts, coincidentally with the experiment, that the mass rate is a parabolic function of the radius. At null evaporation rate and zero surface viscosity, the drop radius is proportional to the Tolman "length" or to the radius of action of the molecular forces. This indicates that at this level the differences between a liquid and a gas cease to exist.

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