

A Model for Droplet Evaporation

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How to cite this paper: Mohazzabi, P., Richardson, G.A. and Richardson, G.A. (2023) A Model for Droplet Evaporation. *Journal of Applied Mathematics and Physics*, 11, 1837-1845.
<https://doi.org/10.4236/jamp.2023.117118>

Received: June 5, 2023

Accepted: July 14, 2023

Published: July 17, 2023

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Abstract

Based on the kinetic theory of gases, a simple model for droplet vaporization, in particular mercury, is developed to study the variation of droplet radius as a function of time. This model is in agreement with more sophisticated models for water, such as the kinetic model and the Kulmala model. Findings indicate that complete evaporation of a 1-mm-radius mercury droplet, in a ventilated room at normal temperatures, should take about 1.8×10^4 seconds or 5 hours. The findings of this study can be utilized to direct further research in the field of toxin remediation.

Keywords

Evaporation, Rate, Mercury, Droplet, Radius

1. Introduction

It is a well-known fact that mercury is a toxic heavy metal. In particular, due to its relatively high vapor pressure at room temperature, droplets of mercury can produce high levels of mercury vapor in the air, inhalation of which can have serious health implications. In fact, in a dark room under black light, one can observe fumes of mercury rising from its liquid, which is quite frightening. Nevertheless, cleaning a spill of mercury caused by various accidents, such as breaking a mercury incandescent light bulb or a mercury thermometer, is not an easy task. This is because one should not simply clean up a mercury spill or mercury droplets by using a vacuum cleaner. A mercury spill must be cleaned-up professionally which can be quite expensive.

The issue of a mercury spill and its toxicity motivated the authors of this article to look into the evaporation rate of small mercury droplets. The question, more specifically, that the authors of this article sought to investigate was how long would it take for mercury droplets to completely vaporize and disappear, so that an area would be safe again, if a mercury spill occurred in a room that was

well ventilated. To answer this question, we started by examining the evaporation of droplets, in general, into a vacuum or a region of low partial pressures of same liquid.

Although extensive literature exists which discusses the evaporation of liquids, in particular water droplets, few discuss the free evaporation of droplets into a vacuum or into a region of low partial pressure of the same liquid. Therefore, we decided to undertake the task of looking into this problem, and to develop a simple model, based on the kinetic theory of gases to study the variation of droplet radius as a function of time. This study will specifically look at the evaporation of mercury droplets.

2. The Model

Let an ideal gas in a container consists of N molecules, each of mass m , and have a pressure P , a volume V , and a temperature T . The gas molecules constantly collide with one another and with the walls of the container. The number of molecules colliding a unit area of the walls per unit time, is given by [1]

$$J = \frac{n}{4} \langle v \rangle \quad (1)$$

where n is the number of molecules per unit volume, and $\langle v \rangle$ is the average speed of the molecules. The average speed of the molecules, in turn, is given by [1] [2]

$$\langle v \rangle = \sqrt{\frac{8kT}{\pi m}} \quad (2)$$

where k is the Boltzmann constant and m is the molecular mass. Combining Equations (1) and (2), and using $n = N/V$, we obtain

$$J = \frac{N}{4V} \sqrt{\frac{8kT}{\pi m}} = \frac{NkT}{V\sqrt{2\pi mkT}} \quad (3)$$

Finally, using the ideal gas law,

$$pV = NkT \quad (4)$$

we find

$$J = \frac{p}{\sqrt{2\pi mkT}} \quad (5)$$

This is a well-known equation [3] [4] that has been used in a variety of areas, including Knudsen effusion experiments for determination of equilibrium vapor pressure of solids [5]. From Equation (5), one can obtain the isothermal steady-state ratio of molecular fluxes of non-reactive gas mixtures through an orifice into a vacuum [6] [7],

$$\frac{R_1}{R_2} = \frac{p_1}{p_2} \sqrt{\frac{M_2}{M_1}} \quad (6)$$

where R_1 and R_2 are the effusion rates of the two gases, p_1 and p_2 are their partial pressures, and M_1 and M_2 are their corresponding molar masses. For

equal partial pressures, $P_1 = P_2$, this equation reduces to the well-known Graham's law of effusion [1] [2] [8].

2.1. Variation of Droplet Radius with Time

First, consider a condensed phase (liquid or solid) in equilibrium with its own vapor at a given temperature. The vapor molecules constantly strike the surface of the liquid or solid and, at the same time, molecules from the liquid or solid vaporize. According to the condensation-evaporation theory and Langmuir [9], every molecule from the vapor phase that strikes the liquid or solid condenses and, independently, molecules from the condensed phase evaporate. At equilibrium, the rates of condensation and evaporation are equal. Consequently, if the vapor is removed from the system, the liquid or solid will continue to evaporate at almost the same rate, as has been verified experimentally [5]. Therefore, the rate of evaporation of a liquid or solid in, even in a vacuum, is given by Equation (5).

Now, consider a spherical liquid droplet of radius r . According to Ostwald-Freundlich equation [10], the vapor pressure of this droplet p is higher than that of the same liquid with flat surface p_0 (both at the same temperature) according to

$$p = p_0 e^{r_c/r} \quad (7)$$

where the *critical radius* r_c is defined by

$$r_c = \frac{2\gamma V_m}{kT} \quad (8)$$

in which γ is the surface tension of the liquid at temperature T and V_m is the volume associated with one molecule. But since we have

$$V_m = \frac{m}{\rho} \quad (9)$$

where ρ is the density of the liquid, the critical radius can also be written as

$$r_c = \frac{2\gamma m}{\rho kT} \quad (10)$$

Then, Equation (5) reduces to

$$J = \frac{p_0}{\sqrt{2\pi mkT}} e^{r_c/r} \quad (11)$$

The number of molecules N in a spherical droplet is

$$N = \frac{V\rho}{m} = \frac{4}{3}\pi r^3 \frac{\rho}{m} \quad (12)$$

where ρ is the density of the droplet. Therefore, the change in the number of molecules as a result of a change in the radius of the droplet is

$$dN = \frac{4\pi r^2 \rho}{m} dr \quad (13)$$

If this change takes place in a time dt , we have

$$\frac{dN}{dt} = \frac{4\pi r^2 \rho}{m} \frac{dr}{dt} \quad (14)$$

On the other hand, since J in Equation (11) can be written as

$$J = -\frac{1}{A} \frac{dN}{dt} = -\frac{1}{4\pi r^2} \frac{dN}{dt} \quad (15)$$

The negative sign is due to the fact that as molecules vaporize from the droplet, the remaining number of molecules in the droplet N decreases with time. Combining Equations (14) and (15), we find

$$J = -\frac{\rho}{m} \frac{dr}{dt} \quad (16)$$

Finally, using Equation (11), we obtain

$$\frac{dr}{dt} = -\frac{p_0}{\rho} \sqrt{\frac{m}{2\pi kT}} e^{r_c/r} \quad (17)$$

which is a first-order nonlinear differential equation for the radius of the droplet as a function of time.

Separating the variables in Equation (17), gives

$$e^{-r_c/r} dr = -\frac{p_0}{\rho} \sqrt{\frac{m}{2\pi kT}} dt \quad (18)$$

Then dividing both sides of the equation by r_c , we find

$$e^{-r_c/r} d\left(\frac{r}{r_c}\right) = -\frac{p_0}{\rho r_c} \sqrt{\frac{m}{2\pi kT}} dt \quad (19)$$

The left hand side of this equation is dimensionless, as is the right hand side. Therefore, the reciprocal of the coefficient of dt on the right hand side must have the dimension of time. We define this quantity as the *critical time* t_c of the system, which upon using Equation (10) reduces to

$$t_c = \frac{\gamma}{p_0} \sqrt{\frac{8\pi m}{kT}} \quad (20)$$

Therefore, Equation (19) becomes

$$e^{-r_c/r} d\left(\frac{r}{r_c}\right) = -d\left(\frac{t}{t_c}\right) \quad (21)$$

We now define the dimensionless radius u and dimensionless time τ by

$$u = \frac{r}{r_c} \quad \text{and} \quad \tau = \frac{t}{t_c} \quad (22)$$

which reduces Equation (21) to the dimensionless form,

$$\frac{du}{d\tau} = -e^{1/u} \quad (23)$$

2.2. Solution of the Differential Equation

Although Equation (23) can be integrated analytically, the solution will be in terms of the exponential integral function [11] [12],

$$Ei\left(-\frac{1}{u}\right) + ue^{-1/u} + \tau = \text{constant} \quad (24)$$

which is not simpler than solving it numerically. Therefore, we choose to solve differential Equation (23) numerically using the 4th-order Runge-Kutta algorithm [13]. We start with the initial condition $\tau = 0$ and $u = 1$, in steps of $\Delta\tau = 0.001$ until $u = 0$. The dimensionless graph of the solution is shown in **Figure 1**. The functional form of this graph is in excellent agreement with those obtained from more sophisticated models for water, such as the kinetic model and the Kulmala model [14] as well as the experimental data [15].

Values of the critical time (t_c) and critical radius (r_c) for some common liquids at 25°C are listed in **Table 1** for reference. Since the value of r_c is typically very small, of the order of a few nanometers, the graph in **Figure 1** shows variation of the droplet radius versus time for very small droplets, shortly before they disappear.

For larger droplets, in particular, when $r \gg r_c$, we have $u \gg 1$, $e^{1/u} \approx 1$ and Equation (23) reduces to

$$\frac{du}{d\tau} = -1 \quad (25)$$

Using the definitions of u and τ (22), this equation becomes

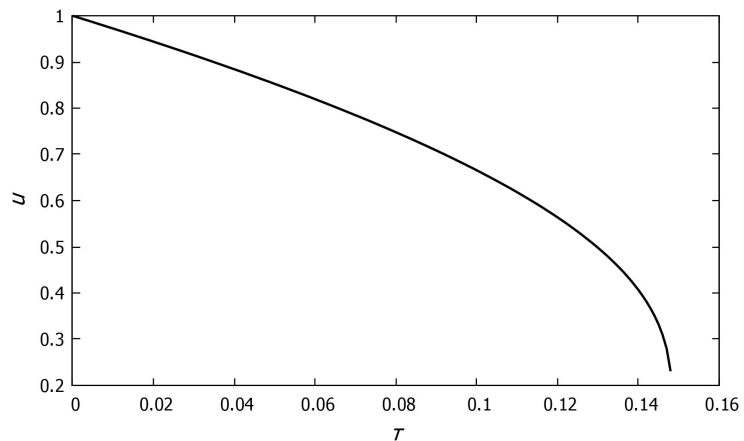


Figure 1. A dimensionless graph of droplet radius as a function of time during free evaporation of the droplet into vacuum.

Table 1. Values of the critical radius (r_c) and critical time (t_c) for some liquids at 25°C. The data for calculations are obtained from various Internet references [16]-[26].

Liquid	r_c (m)	t_c (s)	r_c/t_c (m/s)
Water	1.05×10^{-9}	3.07×10^{-7}	3.42×10^{-3}
Ethanol	1.04×10^{-9}	6.07×10^{-8}	1.71×10^{-2}
Methanol	7.20×10^{-10}	2.35×10^{-8}	3.06×10^{-2}
Ethylene Glycol	2.13×10^{-9}	9.67×10^{-5}	2.20×10^{-5}
Mercury	5.82×10^{-9}	8.89×10^{-5}	6.55×10^{-5}

$$dr = -\frac{r_c}{t_c} dt \tag{26}$$

integration of which, with $r = r_0$ at $t = 0$, gives

$$r = r_0 - \frac{r_c}{t_c} t \tag{27}$$

Therefore, during free-surface evaporation, the radius of a droplet decreases linearly with time until it becomes very small (nanometer size), after which the droplet very quickly evaporates and disappears according to the graph in **Figure 1**. Note that the values of r_c/t_c for Equation (27) can be calculated either from the quantities in the second and third columns of **Table 1**, or directly from

$$\frac{r_c}{t_c} = \frac{p_0}{\rho} \sqrt{\frac{m}{2\pi kT}} \tag{28}$$

which is obtained from dividing Equation (10) by (20). The advantage of using this equation is that it eliminates the need for the values of surface tension.

To calculate the time that it takes a large droplet to completely vaporize, we only use the linear regime described by Equation (27). The justification for this choice is that after the radius of the droplet decreases to the order of r_c , it evaporates in a very short time, of the order of $10^{-7} - 10^{-5}$ seconds as can be seen from **Table 1** which is negligible compared to the linear regime time. **Figure 2** shows the graphs of Equation (27) for evaporation of the liquids droplets shown in **Table 1**.

Equation (5) and hence (23) assume free surface evaporation of the liquid droplet, *i.e.*, evaporation into vacuum. When a droplet evaporates into air at normal pressures, and in some cases involving humidity [14], most of the evaporating molecules are reflected back into the droplet shortly after evaporation as a result of intermolecular collisions between the evaporating molecules and the gas molecules. This happens in the vicinity of the droplet as a result of very high frequency of collisions, which is of the order of 10^{10} s^{-1} [4]. Therefore, the right hand sides of Equations (5) and (23) should each be multiplied by a *reflection factor*, $\alpha < 1$,

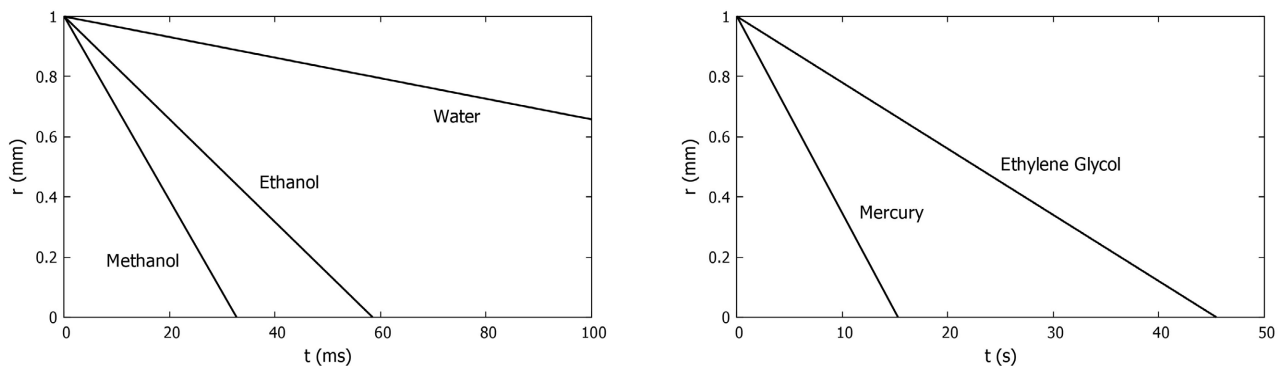


Figure 2. Graphs of droplet radius versus time [Equation (27)] for the liquids listed in **Table 1**. Note that the time scale for ethylene glycol and mercury is seconds but for the other liquids is milliseconds.

Table 2. Average values of the measured evaporation times (t_{eva}) for the liquids listed in **Table 1** (except mercury) and the corresponding reflection factors α .

Liquid	t_{eva}	α
Water	5.0 min	9.7×10^{-4}
Ethanol	65.7 sec	8.9×10^{-4}
Methanol	40.0 sec	8.2×10^{-4}
Ethylene Glycol	16 hr	7.9×10^{-4}

$$J = \frac{\alpha p}{\sqrt{2\pi mkT}} \quad (29)$$

which carries through the calculations and the differential Equation (23) becomes

$$\frac{du}{d\tau} = -\alpha e^{1/u} \quad (30)$$

Consequently, Equation (27) becomes

$$r = r_0 - \alpha \frac{r_c}{t_c} t \quad (31)$$

3. Comparison with Experimental Results

We measured the actual evaporation time (t_{eva}) for droplets of about 1 mm radius of the liquids listed in **Table 1** (except mercury). From these evaporation times and using the following relation,

$$0 = r_0 - \alpha \left(\frac{r_c}{t_c} \right) t_{eva} \rightarrow \alpha = \frac{r_0}{\left(\frac{r_c}{t_c} \right) t_{eva}} \quad (32)$$

with $r_0 = 1$ mm, we calculated the value of reflection factor for each of the liquids. The average value of these measured evaporation times as well as the reflection factors are listed in **Table 2**. From these values, we obtain an average value of $\alpha = 8.7 \times 10^{-4}$ for the reflection factor. Interestingly, with this value and using the value of r_c/t_c for water from **Table 1**, we find a slope of

$$\alpha \left(\frac{r_c}{t_c} \right) = 8.7 \times 10^{-4} (3.42 \times 10^{-3}) = 2.98 \times 10^{-6} \frac{\text{m}}{\text{s}} \quad (33)$$

which is in agreement with the slope of 2.5×10^{-6} m/s obtained experimentally by Walton [27] for radius versus time of water droplet at 50° (from Figure 5 of this reference).

4. Discussion

The theory developed in this work, which is based on the kinetic theory of gases, including the concept of reflection factor, is in agreement with more sophisticated models for water. It also agrees well with the experimental results for four

of the common liquids at room temperature. The theory predicts the free evaporation time, as well as the evaporation time into air for small droplets of these liquids. It is, therefore, reasonable to assume that the theory is, at least approximately, valid for other liquids.

Returning to the question of evaporation of mercury droplets, which is the main objective of this research, an extensive literature search did not produce any experimental data on evaporation of mercury droplets. However, assuming that the reflection factor for mercury is approximately the same as that for the other liquids studied, and using the value of r_c/t_c for mercury from **Table 1**, we find that at 25°, the evaporation time for a mercury droplet with initial radius of 1 mm is

$$t_{eva} = \frac{r_0}{\alpha(r_c/t_c)} = \frac{0.001}{8.7 \times 10^{-4} (6.55 \times 10^{-5})} = 17548 \text{ s} \quad (34)$$

which is approximately 4.9 hours. Therefore, in the case of a mercury spill, if the area is properly ventilated, the mercury should evaporate in about 5 hours.

Application of the theory developed in this work to estimate the evaporation time of a droplet is important, not only for mercury, but also to estimate the time required for droplets of any liquid toxin to completely evaporate, as issue of potential interest to the field of toxin management and control.

Acknowledgements

This work is supported in part by a URAP grant from the University of Wisconsin-Parkside.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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