International Journal of Heat and Mass Transfer 51 (2008) 3696–3699

Contents lists available at ScienceDirect

International Journal of Heat and Mass Transfer

journal homepage: www.elsevier.com/locate/ijhmt

Technical Note

Evaporation dynamics of sessile liquid drops in still air with constant contact radius

Friedhelm Schönfeld [a,*], Karl-Heinz Graf [b], Steffen Hardt [c], Hans-Jürgen Butt [b]

[a] *Institut für Mikrotechnik Mainz GmbH (IMM), Carl-Zeiss-Strasse 18–20, 55129 Mainz, Germany*
[b] *Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany*
[c] *Institut für Nano- und Mikroprozesstechnik, Leibniz Universität Hannover, Callinstrasse 36, 30167 Hannover, Germany*

ARTICLE INFO

Article history:
Received 18 October 2007
Available online 14 May 2008

Keywords:
Droplet evaporation
Contact line pinning

ABSTRACT

Evaporation of sessile drops *with constant wetting radius* is investigated. In contrast to *constant contact angle* the temporal evaluation of the droplet volume can not be formulated in a closed form. We provide two approximations for initial contact angles below 90° which allow predicting the evaporation dynamics in practice easily. The derived linear approximation is suitable for small initial contact angles with a maximum relative deviation of 1% for contact angles below 30°. Further, we provide a non-linear algebraic approximation with a maximum relative error 0.3% in the entire range of contact angle considered.

1. Introduction

Droplet evaporation plays a vital role in various engineering fields, such as air/fuel-premixing, (biological) crystal growth, painting and inkjet printing, to name a few. Generally, the evaporation of sessile drops can occur in two distinct modes, at a constant contact angle and varying wetting radius or vice versa at a constant wetting radius and varying contact angle. For the former case it is known that $V^{2/3}$ decreases linearly with time, V being the volume of the drop [1]. For the evaporation at constant contact radius, no simple analytical law has been reported. In practice, the two evaporation modes are often intermixed, meaning that in different phases either evaporation with constant contact angle or with constant wetting radius occurs. For the analysis of many heat and mass transfer processes it would be helpful to have a simple yet sufficiently general correlation describing the decrease of droplet volume as a function of time. This would especially be beneficial in models for complex devices or systems that incorporate various sub-processes for which simplified descriptions are needed. Here, we derive two simple analytical approximations for the decrease in volume of a drop evaporating with a fixed three-phase contact line. A linear approximation for contact angles significantly below 90° is provided as well as a simple rational function approximating the volume decrease for larger contact angles with high accuracy. Moreover we show that the total evaporation time for pinned drops is proportional to $V_0^{2/3}$ as in the non-pinned case.

2. Mathematical model

Here, we investigate slow evaporation of minute drops on thermally heavy substrates implying that typical temperature changes are small and can be safely neglected. For spherical drops in air it was experimentally found that the rate of evaporation is proportional to the radius of the drop r [2,3]. The rate of evaporation is the decrease in volume of the drop per unit time, $-\mathrm{d}V/\mathrm{d}t$. If the rate of evaporation is proportional to the radius of the drop then $V^{2/3}$ decreases linearly with time since $V \propto r^3$. In accordance with earlier work [4] Langmuir realized that the evaporation of liquids in still air is limited by the diffusion of the vapor molecules through air (or another background gas). He calculated the rate of evaporation with the diffusion equation in polar coordinates [5]. This $V^{2/3}$ dependence of spherical drop evaporation was later confirmed, theoretically and experimentally [6,7].

For sessile drops, formed like a spherical cap with radius of curvature r and contact angle Θ, Picknett and Bexon calculated the rate of evaporation in still air [1] based on the diffusion equation. They obtained

$$\frac{\mathrm{d}V}{\mathrm{d}t} = -2\pi D \cdot \Delta P \cdot \frac{M}{\rho RT} \cdot f \cdot \left(\frac{3V}{\pi\beta}\right)^{1/3} \tag{1}$$

Here, V is the volume of the liquid drop, D is the diffusion coefficient of the vapor molecules in air, $\Delta P = P_0 - P_\infty$ is the difference between the saturation vapor pressure of the liquid P_0 and the vapor pressure far away from the drop surface P_∞. Picknett and Bexon assumed that P_∞ is lower than the saturation vapor pressure of the liquid. M is its molar mass, ρ is the density of the liquid, R and T are gas constant and temperature, respectively. The radius of curvature r is related to the volume and contact angle Θ (in rad) by

---

[*] Corresponding author. Tel.: +49 (0)6131 990 411; fax: +49 (0)6131 990 305.
E-mail address: schoenfeld@imm-mainz.de (F. Schönfeld).

0017-9310/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ijheatmasstransfer.2007.12.027

Nomenclature

a	radius of circular contact line (m)
D	diffusion coefficient of vapour molecules in the gas phase (m^2/s)
M	molar mass (kg/mol)
ΔP	pressure difference $P_0 - P_\infty$(Pa)
P_0	saturation vapor pressure (Pa)
P_∞	ambient vapor pressure (Pa)
r	spherical cap/drop radius (m)
R	universal gas constant (J/mol K)
t	time (s)
T	temperature (K)
V	drop volume (m^3)

Greek symbols	
α	dimensionless factor
δ	dimensionless factor
ρ	liquid density (kg/m^3)
Θ	contact angle (rad)
τ	droplet evaporation time (s)

Subscript	
0	initial value ($t = 0$)

$$V = \frac{\pi}{3} r^3 \beta \tag{2}$$

with $\beta = (1 - \cos\Theta)^2(2 + \cos\Theta)$ and

$$f = 0.00008957 + 0.6333\Theta + 0.116\Theta^2 - 0.08878\Theta^3 + 0.01033\Theta^4 \quad \Theta > 10^\circ \tag{3a}$$

$$f = 0.6366\Theta + 0.09591\Theta^2 - 0.06144\Theta^3 \quad \Theta < 10^\circ \tag{3b}$$

Picknett and Bexon [1] already showed that for constant contact angle, and thus constant β and f, Eq. (1) can be directly integrated leading to

$$V^{2/3} = V_0^{2/3} - \frac{2C}{3}\frac{f}{\beta^{1/3}} t \quad \text{with} \quad C = 2\pi D \left(\frac{3}{\pi}\right)^{1/3} \frac{M\Delta P}{\rho RT} \tag{4}$$

This is the already mentioned linear decrease of $V^{2/3}$ with time. The total evaporation time $\tau = 3\left(V_0^2\beta\right)^{1/3}/(2Cf)$ is proportional to $V_0^{2/3}$, where V_0 is the initial volume.

Even in the case where P_∞ equals the saturation vapor pressure above a flat liquid vapor interface, droplet evaporation occurs. A droplet has to have a curved surface and as described by Kelvin's equation the vapor pressure of a curved liquid surface is higher than the saturation vapor pressure. For the case of droplet evaporation in saturated vapor and constant contact angle it has been shown that the volume decreases linearly with time and the evaporation time is proportional to the initial drop volume [8].

Evaporation at a constant contact angle is not the only possible mode of evaporation. In many practical applications, e.g. involving the evaporation with dispersed [9–13] or dissolved substances [14–17], drops often evaporate at constant contact radius [18]. For constant contact radius the integration of Eq. (1) is analytically not possible because the contact angle and thus f and β are changing during evaporation. In the following we provide two approximations: a simple linear approximation, which agrees well with the exact solution for low initial contact angles, and a higher order solution, which accounts for the non-linear volume decrease for larger initial contact angles. Moreover, we show that the above mentioned relation for the complete evaporation time $\tau \propto V_0^{2/3}$ holds also in the case of constant wetting radius.

We start by rewriting Eq. (1) using the geometric relation

$$V = \frac{\pi\beta}{3} \cdot \left(\frac{a}{\sin\Theta}\right)^3 \tag{5}$$

where a denotes the contact radius, leading to

$$\frac{dV}{dt} = -2\pi D \cdot \Delta P \cdot \frac{aM}{\rho RT} \cdot \frac{f}{\sin\Theta} \tag{6}$$

2.1. Linear approximation

$f/\sin\Theta$ depends only moderately on the contact angle; from 0.64 at $\Theta = 0^\circ$ it increases to 1.0 at $\Theta = 90^\circ$. In order to derive a linear approximation, we replace the rightmost term in Eq. (6) with a constant, i.e. time-independent factor. Yet, this factor should allow for a certain dependence on the initial contact angle, Θ_0, and we approximate Eq. (6) by

$$\frac{dV}{dt} = -2\pi D \cdot \Delta P \cdot \frac{aM}{\rho RT} \cdot \frac{f(\Theta_0/\alpha)}{\sin(\Theta_0/\alpha)} \tag{7}$$

leading to a linear volume decrease

$$V(t) = V_0 - 2\pi D \cdot \Delta P \cdot \frac{aM}{\rho RT} \cdot \frac{f(\Theta_0/\alpha)}{\sin(\Theta_0/\alpha)} \cdot t \tag{8}$$

Here, α is a dimensionless factor. One straightforward choice is to set $\alpha = 2$, which in fact gives good agreement between Eq. (9) and the numerical solution of Eq. (6) for small initial contact angles ($\Theta_0 < 30^\circ$). In order to minimize the error in the whole range of initial contact angles up to 90° a numerical optimization (Newton's method) is applied yielding $\alpha = 1.6$. For instance, the relative error of the linearly approximated total evaporation time

$$\tau = V_0 \frac{\rho RT}{2\pi aDM\Delta P} \cdot \frac{\sin(\Theta_0/1.6)}{f(\Theta_0/1.6)} \tag{9}$$

is found to be less than 1.5% in the whole range of initial contact angles considered.

2.2. Total evaporation time

To find the general relation between drop volume and time we integrate Eq. (6):

$$t = -\frac{\rho RT}{2\pi DaM\Delta P} \cdot \int_{V_0}^{V} \frac{\sin\Theta}{f} \, dV' \tag{10}$$

Substituting V by Θ using

$$\frac{dV}{d\Theta} = \frac{\pi a^3}{(\cos\Theta + 1)^2} \tag{11}$$

leads to

$$t = \frac{a^2 \rho RT}{2DM\Delta P} \cdot \int_{\Theta}^{\Theta_0} \frac{1}{f} \frac{\sin\Theta'}{(\cos\Theta' + 1)^2} d\Theta' \tag{12}$$

From Eqs. (5) and (12) we see that the relation $\tau \propto V_0^{2/3}$ for the complete evaporation time still holds in the case of constant wetting radius, as mentioned above. For the total evaporation time the integration goes from Θ_0 to 0 and the right hand side of Eq. (12) solely depends on Θ_0. Thus, for a given initial contact angle we have $\tau \propto a^2 \propto V_0^{2/3}$.

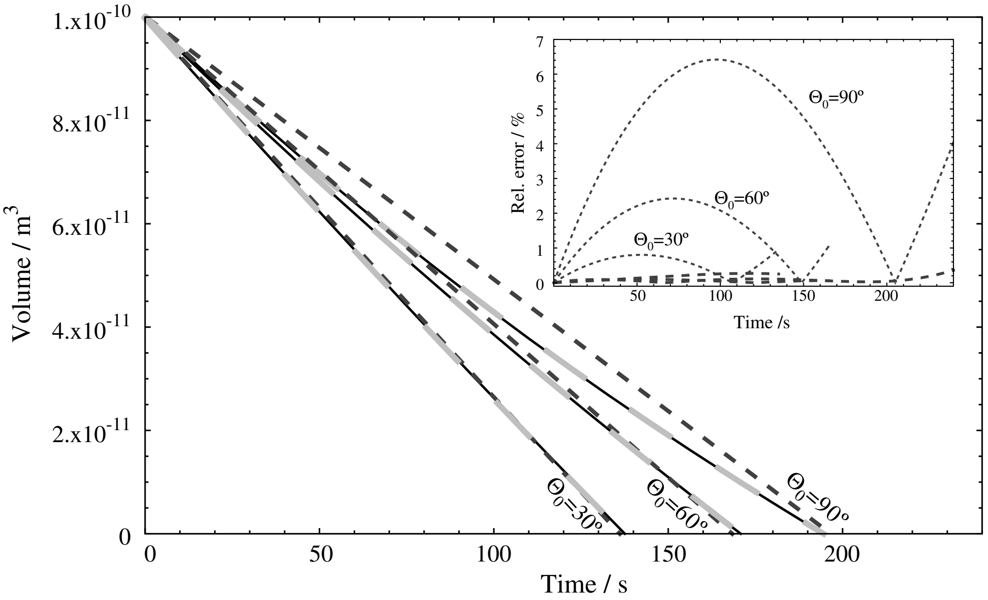

Fig. 1. Volume vs. time for a water drop with an initial volume of $V_0 = 10^{-10}\,\mathrm{m}^3$ (100 nL) evaporating with a constant contact radius at a relative humidity of 50% ($\Delta P = 1585$ Pa because the vapour pressure of water at 25 °C is 3169 Pa). The diffusion coefficient of water molecules in air is $D = 2.4 \times 10^{-5}\,\mathrm{m}^2/\mathrm{s}$. The initial contact angle and the contact radii were 30° and 614 μm, 60° and 463 μm, 90° and 363 μm, respectively. Black solid lines are numerical solutions of Eq. (6). Short-dashed lines denote the linear approximation Eq. (9) for $\alpha = 1.6$. Results obtained with the non-linear approximation Eq. (17) are denoted with long-dashed lines and are indistinguishable from the numerical results in the main plot. Inset: Absolute relative error, that is the volume calculated either with the linear approximation Eq. (9) (short dashed lines) or with Eq. (17) (thick, long dashed) minus the volume calculated numerically and dividing the difference by the initial volume.

2.3. Non-linear approximation

According to Eq. (12), in the general case the time to reach a certain contact angle can be expressed as a difference of two values of a function $g(\Theta)$, i.e., $t \propto g(\Theta_0) - g(\Theta)$, with

$$g(\Theta) = \int_0^{\Theta} \frac{1}{f} \frac{\sin \Theta'}{(1+\cos \Theta')^2}\, \mathrm{d}\Theta' \tag{13}$$

We find that $g(\Theta)$ can be well approximated by

$$g = \left(\frac{3\delta}{\pi} \cdot \frac{\sin^3 \Theta}{\beta} + \frac{1}{4} \right)^{-1} \tag{14}$$

For $\delta = 1.994$ this approximation is found to be accurate within a relative error of less than 1% up to 102°. Moreover, the chosen ansatz allows replacing the angle by the volume, cf. Eq. (5), leading to

$$g = \frac{V}{\delta a^3 + \frac{V}{4}} \tag{15}$$

Inserting Eq. (15) into Eq. (12) and rearranging leads to

$$t \cdot \frac{2DM\Delta P}{a^2 \rho R T} = \frac{V_0}{\delta a^3 + \frac{V_0}{4}} - \frac{V}{\delta a^3 + \frac{V}{4}} \tag{16}$$

Solving Eq. (16) one finds a simple rational function for the volume decrease with time

$$V(t) = \frac{\tau_0 V_0 - 4a^3 \delta \cdot t}{t + \tau_0} \quad \text{with} \quad \tau_0 = \frac{16\delta \rho R T a^5}{2DM\Delta P (4\delta a^3 + V_0)} \tag{17}$$

For a given fixed contact radius Eq. (17) with $\delta = 1.994$ describes the changing volume of the evaporating drop [19].

3. Results and discussion

Fig. 1 summarizes the results showing the decreasing volume of a water drop with an initial volume $V_0 = 10^{-10}\,\mathrm{m}^3$ (100 nL). The temporal change in volume for different contact radii and thus different initial contact angles is plotted. The volume decreases almost linearly with time and can be well described by the linear approximation Eq. (9). Such a linear decrease of the volume with time for pinned contact radius agrees with experimental observations [20,21] and results of finite element simulations [22]. The absolute relative deviation with respect to the initial droplet volume, i.e. $\Delta V/V_0$, where ΔV is the difference of the linearized volume, Eq. (9), and the numerical solution of Eq. (6) are shown in the inset of Fig. 1. The maximum relative errors for $\Theta_0 = 90°$, 60° and 30° are about 6%, 2% and below 1%, respectively. The non-linear approximation Eq. (17) leads to almost indistinguishable results up to initial contact angles of 90°. The relative deviation is found to be below 0.3% in all cases.

Acknowledgement

The work has been supported by the German Research Foundation, DFG-Forschergruppe FOR 516.

References

[1] R.G. Picknett, R. Bexon, The evaporation of sessile or pendant drops in still air, J. Colloid Interface Sci. 61 (1977) 336–350.
[2] B. Sresnewsky, Über die Verdunstung von Flüssigkeiten, Beibl. Ann. Phys. Chem. 7 (1883) 888–890.
[3] H.W. Morse, On the evaporation from the surface of a solid sphere, Proc. Am. Acad. Arts Sci. 45 (1910) 361–367.
[4] J. Stefan, Versuche über die Verdampfung, Sitzungsberichte Akad. Wiss. Wien. 68 (1873) 385–423.
[5] I. Langmuir, The evaporation of small spheres, Phys. Rev. 12 (1918) 368–370.
[6] H.G. Houghton, A study of the evaporation of small water drops, Physics 4 (1933) 419–424.
[7] G.A.E. Godsave, Studies of the combustion of drops in a fuel spray – the burning of single drops of fuel, in: Burning of Fuel Droplets. Fourth Symposium on Combustion, Williams and Wilkins, Baltimore, 1953, pp. 818–830.
[8] H.-J. Butt, D.M. Golovko, E. Bonaccurso, On the derivation of Young's equation for sessile drops: nonequlibrium effects due to evaporation, J. Phys. Chem. B 111 (2007) 5277–5283.
[9] C.D. Dushkin, H. Yoshimura, K. Nagayama, Nucleation and growth of two-dimensional colloidal crystals, Chem. Phys. Lett. 204 (1993) 455–460.

[10] E. Adachi, A.S. Dimitrov, K. Nagayama, Stripe patterns formed on a glass surface during droplet evaporation, Langmuir 11 (1995) 1057–1060.
[11] F. Parisse, C. Allain, Shape changes of colloidal suspension droplets during drying, J. Phys. France II 6 (1996) 1111–1119.
[12] R.D. Deegan, Pattern formation in drying drops, Phys. Rev. E 61 (2000) 475–485.
[13] J. Conway, H. Korns, M.R. Fisch, Evaporation kinematics of polystyrene bead suspensions, Langmuir 13 (1997) 426–431.
[14] T.R. Hebner, C.C. Wu, D. Marcy, M.H. Lu, J.C. Sturm, Ink-jet printing of doped polymers for organic light emitting devices, Appl. Phys. Lett. 72 (1998) 519–521.
[15] T. Kawase, H. Sirringhaus, R.H. Friend, T. Shimoda, Inkjet printing via hole interconnections and resistors for all-polymer transistor circuits, Adv. Mater. 13 (2001) 1601–1605.
[16] Y. Morozumi, H. Ishizuka, J. Fukai, Solute deposit during evaporation of binary liquid micro-droplet on a substrate, in: The International Symposium on Micro-Mechanical Engineering, 2003, pp. 24–30.
[17] B.-J. de Gans, U.S. Schubert, Inkjet printing of well-defined polymer dots and arrays, Langmuir 20 (2004) 7789–7793.
[18] G. Li, H.-J. Butt, K. Graf, Microstructures by solvent drop evaporation on polymer surfaces: dependence on molar mass, Langmuir 22 (2006) 11395–11399.
[19] The linear term of the Taylor-expansion of Eq. 16 in time is found to agree with Eq. 8 within a relative error of less than 1% for $\alpha = 1$. Yet, for practical use we recommend the more compact form Eq. 8 and $\alpha = 1.6$ which is more accurate for larger evaporation times.
[20] K.S. Birdi, D.T. Vu, A. Winter, A study of the evaporation rates of small water drops placed on a solid surface, J. Phys. Chem. 93 (1989) 3702–3703.
[21] S.M. Rowan, G. McHale, M.I. Newton, M. Toorneman, Evaporation of microdroplets of three alcohols, J. Phys. Chem. B 101 (1997) 1265–1267.
[22] H. Hu, R.G. Larson, Evaporation of a sessile droplet on a substrate, J. Phys. Chem. B 106 (2002) 1334–1344.