Droplet evaporation in one-component fluids: Dynamic van der Waals theory

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Abstract – In a one-component fluid, we investigate evaporation of a small axisymmetric liquid droplet in the partial wetting condition on a heated wall at $T \sim 0.9T_c$. In the dynamic van der Waals theory (Phys. Rev. E, 75 (2007) 036304), we take into account the latent-heat transport from liquid to gas upon evaporation. Along the gas-liquid interface, the temperature is nearly equal to the equilibrium coexisting temperature away from the substrate, but it rises sharply to the wall temperature close to the substrate. On an isothermal substrate, evaporation takes place mostly on a narrow interface region near the contact line in a late stage, which is a characteristic feature in one-component fluids.

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Introduction. – The wetting dynamics has been mostly studied for involatile liquids and is not well understood for volatile liquids [1]. A well-known example is evaporation of a liquid droplet on a heated substrate. Here first-order phase transition from liquid to gas occurs on the interface, where latent heat is carried away from the interface with gas flow. For a liquid droplet in air the radius $r_c(t)$ has been observed to decrease as $r_c(t) \sim (t_0 - t)^a$, with $a \geq 0.5$, until it vanishes at time $t_0$ [2–5]. Detailed information of evaporation and contact line motion has been provided by various theoretical approaches [6–12]. In near-critical one-component fluids, in particular, a bubble in liquid was observed to be attracted to a heated wall even when the wall was wetted by liquid in equilibrium [13]. In one-component fluids, the contact angle increases with the heat flux.

In this letter, we numerically study evaporation of a droplet in one-component fluids in the axisymmetric geometry. As an efficient numerical method, we use the dynamic van der Waals model [14], which is a phase field model of fluids with inhomogeneous temperature. The pressure $p$ outside a droplet (or bubble) is nearly homogeneous so that the interface temperature should be close to the equilibrium coexisting (saturation) temperature $T_{ce}(p)$ even in heat flux [14,15]. Thus, near the contact line on a heated or cooled wall, a steep temperature variation and a large heat flux should appear, as theoretically studied by Nikolayev et al. [11,12] and as measured by Höhmann and Stephan [16]. Therefore, the hydrodynamics is singular around the contact line in heat flux. This aspect has not yet been well studied in the literature. On the other hand, in multi-component fluids, the interface temperature changes on the scale of the droplet size and evaporation should take place all over the surface.

Dynamic van der Waals model. – We examine the gas-liquid phase transition in nonstationary, inhomogeneous temperature $T(r,t)$. We start with the entropy functional $S_k$ dependent on the number density $n(r,t)$ and the internal energy density $e(r,t)$ by the functional derivative $1/T = \delta S_k/\delta n$. We assume that $S_k = \int dr \hat{S}$ is the space integral of the entropy density $\hat{S}$ consisting of regular and gradient parts as

$$\hat{S} = ns(n,e) - \frac{1}{2} C |\nabla n|^2,$$

(1)

where $s$ is the entropy per particle dependent on $n$ and $e$. The second term is the gradient entropy density, which is negative and is important near the interface. The coefficient $C$ is assumed to be a constant. In the van der Waals theory, fluids are characterized by the molecular volume $v_0$ and the attractive pair interaction energy $\epsilon$ and

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the entropy $s$ is written as

$$s = k_B \ln[(e/n + \epsilon v_n)^{3/2}(1/v_n - 1)] + s_0,$$

(2)

where $s_0/k_B = \ln[v_0(m/3\pi n^2)^{3/2}] + 5/2$ with $m$ being the molecular mass. In this letter, we assume that the fluid internal energy $\mathcal{E}_0$ is the space integral of $\epsilon$. Then we have the usual relation $1/T = n(\partial s/\partial e)_n$, which yields the well-known expression $\epsilon = 3nk_BT/2 - \epsilon v_n^2$. More generally, we may assume the form $\mathcal{E}_0 = \int \Phi(x) + K|\nabla n|^2/2$, where the second term represents the gradient energy density [14]. In this letter, we set $K = 0$ for simplicity.

We set up the hydrodynamic equations from the principle of positive entropy production in nonequilibrium. No gravity is assumed. The mass density $\rho = mn$ obeys the continuity equation

$$\frac{\partial}{\partial t} \rho = -\nabla \cdot (\rho \mathbf{v}).$$

(3)

The momentum density $\rho \mathbf{v}$ and the total energy density $e_T \equiv e + \rho v^2/2$ are governed by [17]

$$\frac{\partial}{\partial t} \rho \mathbf{v} = -\nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{\Pi} - \mathbf{\sigma}),$$

(4)

$$\frac{\partial}{\partial t} e_T = -\nabla \cdot \left[ e_T \mathbf{v} + (\mathbf{\Pi} - \mathbf{\sigma}) \cdot \mathbf{v} - \lambda \nabla T \right].$$

(5)

Here $\mathbf{\Pi} = \{\Pi_{ij}\}$ is the irreversible stress tensor consisting of the van der Waals pressure $p = k_BTn/(1 - v_n) - \epsilon v_n^2$ and the gradient contribution as

$$\Pi_{ij} = p\delta_{ij} - CT \left[ n\nabla^2 n + \frac{1}{2} |\nabla n|^2 \delta_{ij} - \nabla_i n \nabla_j n \right].$$

(6)

The $\mathbf{\sigma} = \{\sigma_{ij}\} = \eta(\nabla_i v_j + \nabla_j v_i) + (\zeta - 2\eta/3) \nabla \cdot \mathbf{v} \delta_{ij}$ is the viscous stress tensor in terms of the shear viscosity $\eta$ and the bulk viscosity $\zeta$. Hereafter $\nabla_j = \partial/\partial x_j$ with $x_i$ representing $x$, $y$, and $z$. $\lambda$ in eq. (5) is the thermal conductivity.

We note that $\Pi_{ij}$ satisfies $\sum_j \nabla_j (\Pi_{ij}/T) = n
abla_i \hat{\mu} - e
abla_i T^{-1}$, where $\hat{\mu}$ is the generalized chemical potential including the gradient contribution. If $C$ is assumed to be a constant, $\hat{\mu}$ reads

$$\hat{\mu} = T(\delta S_0/\delta n)e = \mu - TC\nabla^2 n,$$

(7)

where $S_0 = \int d\mathbf{r} \dot{S}$ is the entropy functional and $\mu = \mu(T, n)$ is the usual chemical potential. In equilibrium the stress balance $\sum_j \nabla_j \Pi_{ij} = 0$ is equivalent to the homogeneity of $\hat{\mu}$. The interface profile $n = n(x)$ is obtained from $\mu(T, n) - CT\nabla^2 n/dx^2 = \mu_{eq}(T)$, where $\mu_{eq}(T)$ is the chemical potential in two-phase coexistence. This interface equation was derived by van der Waals [18].

In our simulation, however, we solved the equation for the entropy density $\dot{S}$ in eq. (1),

$$\frac{\partial \dot{S}}{\partial t} + \nabla \cdot \left[ \dot{S} \mathbf{v} - Cn(\nabla \cdot \mathbf{v}) \nabla n - \frac{\lambda}{T} \nabla T \right] = \dot{\epsilon}_e + \dot{\epsilon}_\theta/T,$$

(8)

together with the continuity and momentum equations (3) and (4). The right-hand side of eq. (8) is the nonnegative-definite entropy production rate with

$$\dot{\epsilon}_e = \sum_{ij} \sigma_{ij} \nabla_i v_j, \quad \dot{\epsilon}_\theta = \lambda(\nabla T)^2/T.$$
where $\Phi_1$ arises from the short-range interaction between the fluid and the wall assumed to be smooth [1]. We set $\partial n / \partial z = 0$ at $z = H$ and $\partial n / \partial r = -0.1 / v_0 \ell$ at $r = L$. We first placed a hemispheric liquid droplet with radius 100 at $T = 0.875 T_c$, where the liquid and gas densities were those on the coexistence curve given by $n_l = 0.580 / v_0$ and $n_g = 0.122 / v_0$, respectively. We then waited a time interval of 4200 to let the system relax to the true equilibrium, where $T = 0.875 T_c$ throughout the system and $v = 0$ even around the interface, and the pressure difference between the two phases satisfied the Laplace law. The liquid and gas densities attained are $0.581 / v_0$ and $0.123 / v_0$, respectively, which are slightly different from the initial values due to the surface tension effect. In fig. 1, we show such a state with $\Phi_1 = -0.1$, where the contact angle is 135°. At $T = 0.875 T_c$, the contact angle vanishes for $\Phi_1 \approx 0.12$ and the wall is completely wetted by liquid for larger $\Phi_1$. We determine the interface position by $n(r, z) = (n_l + n_g) / 2$. As $z \to 0$ we obtain the position of the contact line $r = r_c$.

**Heating a liquid droplet.** – We prepared an equilibrium state with $\Phi_1 = 0.05$ in the partial wetting condition, where the contact angle is 57°. We then raised the substrate temperature $T_0$ to 0.91 $T_c$, while the temperature $T_H$ at the ceiling was unchanged from 0.875 $T_c$. We set $t = 0$ at this temperature change. The $\Phi_1$ was kept fixed. The contact angle increased up to 67° around $t = 1800$ in accord with the experiment [13], but it slowly decreased afterwards being equal to 60° at $t = 10800$. (These two times correspond to the beginning and middle of a late stage of evaporation in fig. 4 below.) The droplet assumed a cap-like shape until it disappeared.

In fig. 2, the droplet shape and the velocity field are shown at $t = 100$ in an early stage and at $t = 5800$ in a late stage. Evaporation is taking place strongly in the vicinity of the contact line $r = r_c(t)$. In the upper panel of fig. 3, we show the heat flux on the substrate

$$Q_b(r, t) = -\left( \lambda \frac{\partial T}{\partial z} \right)_{z=0} ,$$

at these two times. It exhibits a sharp peak at $r = r_c(t)$, where the wall supplies excess heat needed for evaporation. This behavior is in accord with the theoretical result by Nikolayev et al. [11]. In the lower panel of fig. 3 at $t = 5800$, the temperature $T$ is nearly constant along the
the contact line is then given by \( T = T_{\text{c}} \) equal to the coexistence temperature at the contact line \( r = r_0(t) \). Lower panel: profile of \( T(r,z,t)/T_c \) at \( t = 5800 \). It sharply drops to 0.8815 near the contact line \((r = r_0(t) \text{ and } z = 0)\), where evaporation occurs strongly.

![Fig. 3: Upper panel: heat flux \( Q_b(r,t) \) on a heated substrate in units of \( e\ell/v_{070} \) at \( t = 100 \) and 5800 with a sharp maximum at the contact line \( r = r_0(t) \). Lower panel: profile of \( T(r,z,t)/T_c \) at \( t = 5800 \). It sharply drops to 0.8815 near the contact line \((r = r_0(t) \text{ and } z = 0)\), where evaporation occurs strongly.](image)

In the second line we set \( \lambda_t = k_B n_0 n_t \) and \( \Delta s \sim k_B \). This estimation is consistent with the numerical values of \( v_g \) in fig. 2. We also changed \( \Delta T \) and confirmed the linear relationship \( v_g \propto \Delta T \) in the partial-wetting condition.

In fig. 4, we display the radius of the contact line \( r_c(t) \) vs. \( t \). In the early stage \( t \lesssim 10^3 \), \( r_c(t) \) decreases rapidly, where evaporation takes place strongly all over the surface (see fig. 5 below). In the late stage \( t \gtrsim 10^5 \), it decreases algebraically as

\[
r_c(t) \propto (t_0 - t)^{0.42},
\]

until it disappears at \( t_0 \geq 2 \times 10^4 \). The exponent 0.42 in eq. (15) is smaller than the exponent 0.5 for macroscopic droplets in air [2–4]. The droplet volume decreased as \((t_0 - t)^{1.12}\) and the average droplet density \( \bar{n}(t) \) slowly decreased roughly as \( \bar{n} \sim n_0 \propto (t_0 - t)^{0.08} \). The latter is because the droplet interior is gradually heated, as can be seen from the inhomogeneous temperature profile in fig. 3. The interior density approaches the gas density before its disappearance. The droplet interior thus changes in a complicated manner and we cannot present clear explanations of the exponents 0.42, 1.12, and 0.08 at present.

**Evaporation rate.** We next examine the evaporation rate. To this end we introduce the mass flux through the interface,

\[
J = n(\nu - \nu_{\text{int}}) \cdot \nu,
\]

where \( \nu = -|\nabla n|^{-1}\nabla n \) is the normal unit vector at the surface from liquid to gas and \( \nu_{\text{int}} \cdot \nu \equiv \partial r_c(t)/\partial t \) is the interface velocity. If \( J \) is regarded as a function of the coordinate along the normal direction \( \nu \), it is continuous through the interface from the mass conservation, while \( n \) and \( \nu \cdot \nu \) change discontinuously. Thus we may determine \( J = J(r,t) \) on the interface as a function of \( r \) at each time.

In the thin interface limit \( J \) is related to the discontinuity...
Fig. 5: Evaporation rate $W_{\text{tot}}^c$ on all the interface in eq. (18) and that $W_{\text{con}}^c$ in the vicinity of the contact line $r_c - 6\ell < r < r_c$ in eq. (19) in units of $\ell /
u_0 t_0$ vs. $t$ until disappearance of the droplet. Evaporation occurs all over the interface in an early stage after heating the substrate, but it mostly occurs at the contact line in a late stage. Inset: evaporation rates in the early stage, where sound propagation in liquid gives rise to oscillatory relaxation.

of the heat flux $-\lambda \cdot \nabla T$ as

$$T \Delta s J - \nu \cdot [\lambda (\nabla T)_{\text{gas}} - \lambda (\nabla T)_{\text{liq}}] = 0,$$

(17)

from the energy conservation at the interface, where the subscript gas (liq) denotes the value in the gas (liquid) side close to the interface. The total evaporation rate $W_{\text{tot}}^c$ is the surface integral of $J$. The surface area in the range $[r, r + dr]$ is $2\pi dr r / \sin \theta$, where $\theta$ is the angle between $\nu$ and the $r$ axis. Thus,

$$W_{\text{tot}}^c = 2\pi \int_0^{r_c} \sin \theta d r J r.$$

(18)

The particle number within the droplet $N_d$ decreases in time as $d N_d / dt = -W_{\text{tot}}^c$. The droplet volume $V_d$ is related to $N_d$ by $V_d = V_d / \bar{n}$ in terms of the average droplet density $\bar{n}$ and is proportional to $r_c^3$ for thick droplets. We also define the evaporation rate near the contact line

$$W_{\text{con}}^c = 2\pi \int_{r_c - r_w}^{r_c} \sin \theta d r J r.$$

(19)

Here we set $r_w = 6\ell$, which is twice longer than the interface width and remains shorter than $r_c$ before the droplet disappearance. In fig. 5, we show $W_{\text{tot}}^c(t)$ and $W_{\text{con}}^c(t)$ vs. $t$. The two curves nearly coincide for $t \geq 10^3$. This demonstrates that evaporation occurs only near the contact line at long times. Also in fig. 3, along the interface far from the substrate $z \gg \xi$, we can see $\nu \cdot \nabla T = 0$ and recognize $J = 0$ from eq. (17). In terms of $v_g$ in eq. (14) we then obtain

$$W_{\text{tot}}^c \sim 2\pi \xi r_c n_g v_g.$$

(20)

If the droplet density is treated as a constant ($= n_c$), eqs. (14) and (21) yield

$$\frac{d}{dt} r_c^2 \sim -W_{\text{tot}}^c / r_c n_c$$

$$\sim -\lambda \Delta T / T_{\text{liq}} n_c \Delta s,$$

(21)

which is consistent with the curve in fig. 4 at long times $t \geq 10^3$. The agreement with the decay behavior (15) becomes better if we account for the slow decrease of the droplet density (see the discussion below eq. (15)).

As shown in the inset of fig. 5, $W_{\text{tot}}^c$ is much enhanced exhibiting oscillatory behavior on the acoustic time scale (of the order of the droplet radius divided by the liquid sound velocity), where evaporation takes place all over the interface. The sound velocity is 5.43 in liquid and 2.67 in gas in units of $\ell / t_0$ with $\sigma = 0.06$ at $T = 0.875T_c$, so the acoustic disturbances propagate faster in liquid. Before the first peak of $W_{\text{tot}}^c$, a compression sound pulse emitted from the substrate adiabatically warms the liquid [23,24], resulting in a rapid rise of evaporation on all the interface. Its subsequent sharp drop at $t \sim 7$ then occurs with propagation of an expansion sound wave emitted from the contact line, where evaporation suddenly starts and cools...
the surrounding liquid. These acoustic waves are mixed after the first minimum.

**Leidenfrost effect.** – In fig. 6, we show an extreme case of heating the substrate from 0.875Tc to 0.975Tc at t = 0. Here, at the pressure in the gas, the substrate temperature is much above Tc at the first minimum. On a time scale of order 100, a gas layer emerges on the substrate and it supports a large temperature gradient. Here the whole liquid layer adjacent to the heater turns simultaneously into the gas. The droplet is then detached from the substrate (the Leidenfrost effect). Without gravity in this case, the droplet slowly moves towards the cooler boundary and the droplet interior becomes cooler than the surrounding gas region due to evaporation. It eventually collides with the cooler boundary to form a thickened wetting layer (see fig. 7 of our previous paper [14]). In gravity, a droplet may be suspended in gas in a steady state. On the other hand, a gas bubble is attracted to a warmer boundary [13,14]. The lower panel of fig. 6 demonstrates that the temperature is nearly homogeneous all along the interface at Tc(x) with disappearance of the contact line. Here the temperature in the gas layer between the droplet and the substrate steeply changes from $T_0$ to $T_c(x)$. Thus the layer is strongly absorbing heat from the substrate.

**Summary and concluding remarks.** – For one-component fluids we have examined evaporation of a small droplet on a heated smooth substrate in the partial wetting condition in the axisymmetric geometry. In the dynamic van der Waals theory [14], we have integrated the entropy equation (8) together with the continuity and momentum equations to avoid parasitic flow around the interface. Our system length is of the order of several ten nanometers if the mesh length $\Delta x$ is a few Å.

In our simulation, the temperature exhibits a sharp drop near the contact line, leading to a large temperature gradient and a large heat flux localized near the contact line. As is evident in fig. 5, evaporation in one-component fluids occurs only near the contact line at long times. Here we should note that we have assumed the isothermal boundary condition on the substrate. For finite thermal conductivity of the wall, however, the substrate temperature is lowered at the contact line and the temperature drop to $T_c(x)$ in the fluid should become much more gradual near the contact line [11,12,16].

Phenomenologically, the evaporation rate of a thin liquid droplet in air has been assumed to be of the form [2–4],

$$J(r, t) = J_0 / \sqrt{r_c(t)^2 - r^2}. \quad (22)$$

Here $J_0$ is a constant, but its expression in terms of the physical parameters remains unknown. The total evaporation rate $W_{\text{tot}}$, which is the surface integral of $J(r, t)$, is proportional to $r_c$, as in our case in eq. (20). If the temporal decrease of the liquid density is neglected, the above $J(r, t)$ yields $r_c(t) \propto (t_0 - t)^{0.5}$ in agreement with the experiments [2–4]. This decay law is analogous to that in eq. (21) for one-component fluids, although the forms of $J(r, t)$ in the two cases are very different. In multi-component fluids, a velocity field induced by the Marangoni effect should serve to realize evaporation on all the interface [9,10].

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**REFERENCES**

[1] de Gennes P. G., *Rev. Mod. Phys.*, 57 (1985) 827.
[2] Deegan R. D., Bakajin O., Dupont T. F., Huber G., Nagel S. R. and Witten T. A., *Nature*, 389 (1997) 827.
[3] Guéna G., Poulard C. and Cazabat A. M., *Colloid Interface Sci.*, 312 (2007) 164.
[4] Shahidzadeh-Bonn N., Rafai S., Azouni A. and Bonn D., *J. Fluid Mech.*, 549 (2006) 307.
[5] Butt H. J., Glovko D. S. and Bonaccurso E., *J. Phys. Chem B*, 111 (2007) 5277.
[6] Anderson D. M. and Davis S. H., *Phys. Fluids*, 7 (1995) 248.
[7] Koplik J., Pal S. and Banavar J. R., *Phys. Rev. E*, 65 (2002) 021504.
[8] Brient A. J., Wagner A. J. and Yeomans J. M., *Phys. Rev. E*, 69 (2004) 031602.
[9] Savino R. and Fico S., *Phys. Fluids*, 16 (2004) 3738.
[10] Hu H. and Larson R. G., *Langmuir*, 21 (2005) 3972.
[11] Nikolayev V. S., Beysens D. A., Lagier G. L. and Hegiseth J., *Int. J. Heat Mass Transfer*, 44 (2001) 3499.
[12] Nikolayev V. S., preprint (arXiv:0709.4631).
[13] Hegiseth J., Oripsan A., Garrabos Y., Nikolayev V. S., Lecoutre-Chabot C. and Beysens D., *Phys. Rev. E*, 72 (2005) 031602.
[14] Onuki A., *Phys. Rev. E*, 75 (2007) 036304.
[15] Onuki A. and Kanatani K., *Phys. Rev. E*, 72 (2005) 066304.
[16] Höhmann C. and Stephan P., *Exp. Thermal Fluid Sci.*, 26 (2002) 157.
[17] Landau L. D. and Lifshitz E. M., *Fluid Mechanics* (Pergamon) 1959.
[18] Rowlinson J. S., *J. Stat. Phys.*, 20 (1979) 197.
[19] Lafaure B., Nardone C., Scardovelli R., Zaleski S. and Zanetti G., *J. Comput. Phys.*, 113 (1994) 134.
[20] Jamet D., Torres D. and Brackbill J. U., *J. Comput. Phys.*, 182 (2002) 262.
[21] Shin S., Abdel-Khalik S. I., Daru V. and Juric D., *J. Comput. Phys.*, 203 (2005) 493.
[22] Bird R. B., Stewart W. E. and Lightfoot E. N., *Transport Phenomena* (Wiley, New York) 2002, p. 272.
[23] Miura Y., Yoshihara S., Ohnishi M., Honda K., Matsutomo M., Kawai J., Ishikawa M., Kobayashi H. and Onuki A., *Phys. Rev. E*, 74 (2006) 010101(R).
[24] Onuki A., *Phys. Rev. E*, 76 (2007) 061126.