Vapor-Induced Motion of Liquid Droplets on an Inert Substrate

Xingkun Man$^{1,2,*}$ and Masao Doi$^{1,2,†}$

$^{1}$Center of Soft Matter Physics and its Applications, Beihang University, Beijing 100191, China
$^{2}$School of Physics and Nuclear Energy Engineering, Beihang University, Beijing 100191, China

Abstract

Evaporating droplets are known to show complex motion that has conventionally been explained by the Marangoni effect (flow induced by the gradient of surface tension). Here, we show that the droplet motion can be induced even in the absence of the Marangoni effect due to the gradient of evaporation rate. We derive an equation for the velocity of a droplet subject to non-uniform evaporation rate and non-uniform surface tension placed on an inert substrate where the wettability is uniform and unchanged. The equation explains the previously observed attraction-repulsion-chasing behaviors of evaporating droplets.

---

* Email: manxk@buaa.edu.cn
† Email: masao.doi@buaa.edu.cn
Evaporating droplets show complex motion that has attracted abiding interest in scientific research since the early work of Leidenfrost who observed chaotic motion of water droplets on a hot skillet [1]. Equally complex motion of droplets (attraction, repulsion, chasing etc) has been reported for volatile droplets slowly evaporating at room temperature [2–7], but, apart from the conjecture that the phenomena is caused by the Marangoni effect (flow induced by the gradient of surface tension), no quantitative theory has been given.

Cira et al [7] reported that evaporating droplets show complex motion even if they are placed on an inert substrate where the wettability is uniform and unchanged. Figure 1 schematically shows their results for the case of pure liquid droplets. Here, droplets made of pure water (W) and polypropylene glycol (PG) are evaporating on a solid substrate. The left droplet is mobile and the right droplet is pinned. They reported that W moves away from PG (Fig. 1b), but PG moves toward W (Fig. 1c), (hence they chase each other when both droplets are mobile). On the other hand, same droplet pair (W-W and PG-PG) always attract each other (Fig. 1a and d).

Such motion of evaporating droplets has conventionally been explained by the vapor-mediated Marangoni effect [3–7]. Liquid vapor evaporating from one droplet condenses in other droplets and changes the local composition of the droplet (see Fig. 1e). Since the vapor density is not uniform (the vapor density is high near the droplet and decreases with the distance $r$ from the droplet), this creates a non-uniform surface tension in the droplet, and causes a Marangoni flow leading to the droplet motion.

The Marangoni effect can explain the observed motion of two droplets made of different kinds of liquids (W-PG), but cannot explain the motion of two droplets of same pure liquid (W-W or PG-PG) since there should be no Marangoni effect in this case.

The effect of non-uniform vapor density is not limited to the Marangoni effect. If the vapor density is not uniform, the evaporation rate of the droplet becomes non-uniform [7–10]. This effect is important for the the droplets of same pure liquid as it is the only mechanism for the vapor-mediated interaction between them.

Non-uniform evaporation of the liquid induces internal fluid flow, and thus deforms the droplet. Daniel et al [11] have pointed out that such shape deformation actuates the motion of the droplet due to the gradient of the Laplace pressure, but this effect (called Capillary effect by Brenner et al [12]) has not been analysed theoretically.

In the following we consider the motion of a droplet placed on a substrate and in non-
FIG. 1. (a)-(d) Schematic pictures of the directional motions of two neighbouring droplets reported by Cira et al, Nature 519, 446 (2015). Blue droplet denotes a pure water (W) and yellow droplet denote a pure propylene glycol (PG). In all figures, the right droplet is pinned, while the left one is free. (a) Two W droplets attract each other; (b) A pinned PG droplet repels a free W droplet; (c) A pinned W droplet attracts a free PG droplet; (d) Two PG droplets attract each other. (e) The problem discussed in this article: how a droplet which has asymmetrical liquid/vapor surface tension moves when it is placed in a non-uniform vapor environment.

uniform vapor density (see Fig. 1e). To avoid complications, here we assume that the substrate is inert: the wettability of the substrate is uniform and is not affected by the vapor. If the wettability changes, it will creates the motion of a droplet. This problem has been extensively studied both experimentally [13–17] and theoretically [18, 19], and can be easily included in the present theory.

Due to the non-uniform vapor density, the evaporation rate $J$ and the liquid/vapor surface tension $\gamma$ are not uniform. Here we assume that the gradients of $J$ and $\gamma$ are small and have $x$-component only:

$$J = J_0 + \frac{\partial J}{\partial x} [x - x_c(t)],$$

$$\gamma = \gamma_0 + \frac{\partial \gamma}{\partial x} [x - x_c(t)],$$

(1)

(2)
where \( x_c(t) \) is the center of the contact line of the droplet, and \( J_0 \) and \( \gamma_0 \) are the mean evaporation rate and the surface tension.

To determine the motion of this droplet, we use the Onsager principle \([20, 21]\). This principle is equivalent to the variational principle known in Stokesian hydrodynamics for moving boundary problem: the motion of moving boundaries is determined by the condition that the Rayleighian \( \mathfrak{R} = \Phi + \dot{F} \) be minimum with respect to the boundary velocity, where \( \Phi \) is the energy dissipation function (the half of the energy dissipation rate created in the fluids by the boundary motion), and \( \dot{F} \) is the change rate of the free energy. The principle has been applied for the droplet motion by gravity \([22]\) and by evaporation \([23]\).

To use this principle, we assume that the surface profile of the droplet is given by (in a cylindrical coordinate)

\[
h(r, \varphi, t) = H(t) \left[ 1 - \frac{r^2}{R(t)^2} \right] \left[ 1 + \alpha(t) r \cos \varphi \right],
\]

where \( H(t) \) and \( R(t) \) are the height and the radius of the droplet, and \( \alpha(t) \) is a parameter describing the shape deformation of the droplet. The state of the droplet is specified by four parameters \( H(t), R(t), \alpha(t) \) and \( x_c(t) \). We shall determine the time evolution of these parameters by the Onsager principle.

We assume that the droplet is nearly flat \([R(t) \gg H(t)]\) and use the lubrication approximation to calculate the dissipation function:

\[
\Phi(\mathbf{v}_f) = \frac{1}{2} \int_0^R \int_0^{2\pi} \frac{3\eta v_f^2 r dr d\varphi}{h},
\]

where \( \eta \) is the viscosity of the fluid and \( \mathbf{v}_f(r, \varphi) \) is the height averaged velocity of the fluid at point \((r, \varphi)\). Therefore, the model is valid when the droplet contact angle and the fluid Reynolds number are small, i.e. \( \theta \ll 1 \) and \( Re \ll 1 \). The velocity is determined by the minimum of \( \Phi(\mathbf{v}_f) \) under constraint that \( \mathbf{v}_f \) satisfies the conservation equation \( \dot{h} = -\nabla \cdot (\mathbf{v}_f h) - J \).

The calculation of \( \mathbf{v}_f \) becomes simple in the special case that the droplet remains undeformed [i.e, \( \alpha(t) \) remains to be zero]. In this case, the \( x \) component of \( \mathbf{v}_f \) is given by

\[
v^x_f = v_0 + \dot{x}_c + \frac{R^2}{2H} \frac{\partial J}{\partial x},
\]

where \( v_0 \) stands for the velocity induced by \( J_0 \) and is independent on \( \dot{x}_c \). Inserting this expression into Eq. (4), \( \Phi \) is calculated as

\[
\Phi = \Phi_0 + \frac{3\pi C \eta R^2}{H} \dot{x}_c^2 + \frac{3\pi C \eta R^4}{2H^2} \frac{\partial J}{\partial x} \dot{x}_c.
\]
where $\Phi_0$ represents the term arising from $v_0$ and is independent of $\dot{x}_c$, and $C$ is a dimensionless constant given by $C = \ln (R/2\epsilon)$ where $\epsilon$ is the molecular cutoff length that is introduced to remove the divergence in the energy dissipation at the contact line.

The rate of the free energy change $\dot{F}$ has two parts: the capillary effect, $\dot{F}_C$, and the Marangoni effect, $\dot{F}_M$. $\dot{F}_C$ is independent of $\dot{x}_c$, while $\dot{F}_M$ is written as

$$\dot{F}_M = -\int_0^R \int_0^{2\pi} v_s \cdot \nabla \gamma r dr d\varphi = -\frac{3\pi R^2}{2} \frac{\partial \gamma}{\partial x} \dot{x}_c,$$

(7)

where $v_s$ is the fluid velocity on the liquid/vapor interface, which is related to $v_f$ by $v_s = \frac{3}{2} v_f + \frac{(\partial \gamma/\partial x)}{4} h/\eta$.

By minimizing the Rayleighian $\Re = \Phi + \dot{F}$ with respect to $\dot{x}_c$, we obtain the velocity of the droplet induced by the gradients of surface tension and evaporation rate:

$$\dot{x}_c = \frac{R\theta}{4\eta C} \frac{\partial \gamma}{\partial x} - \frac{R}{\theta} \frac{\partial J}{\partial x},$$

(8)

where $\theta(t) = 2H(t)/R(t)$ is the contact angle (see the Supplemental Material for the full derivation).

Equation (8), indicates that non-uniform surface tension $\partial \gamma/\partial x$ moves the droplet from low surface tension side to high surface tension side. This conclusion is consistent with the understanding that droplet moves in the same direction as the Marangoni flow which is in the direction toward the high surface tension side (see Fig. 2a).

Equation (8) also indicates that the non-uniform evaporation rate $\partial J/\partial x$ moves the droplet from high evaporation side to low evaporation side (evaporation effect). This result can be understood by the minimum energy dissipation principle in Stokesian hydrodynamics. Consider the case of $\partial J/\partial x > 0$ (see Fig. 2b), the liquid on the right side of the droplet evaporates faster than that on the left side. To maintain the symmetric parabolic shape given by Eq. (3) with $\alpha = 0$, fluid flow is created in the droplet. If the contact line is fixed, this fluid flow is from left to right. However, if the contact line is mobile, the motion of the droplet takes place from right to left to reduce the energy dissipation associated with this fluid flow.

For a pair of same pure liquid droplets, $\partial \gamma/\partial x$ is zero, while $\partial J/\partial x$ is non zero. Since the evaporation rate is lower in the middle of the pair than at the edge, $\partial J/\partial x$ is negative for the left droplet and positive for the right one. Accordingly, they always approach each other.
FIG. 2. (a-b) Schematic pictures of theoretical results for the motion of liquid droplet induced by non-uniform surface tension (a) and by non-uniform evaporation (b). (c-e) Calculated time evolution of the droplet interface between the liquid and vapor, $h(x, y = 0, t)/H_0$. Here $H_0$ and $R_0$ are the initial value of $H(t)$ and $R(t)$, and the dimensionless surface tension gradient $\beta_S$ and the evaporation rate gradient $\beta_J$ (defined in the text) are given by (c): $\beta_S = -0.2$, $\beta_J = 1.0$, (d): $\beta_S = 0.4$, $\beta_J = 0.5$, and (e): $\beta_S = 2.0$, $\beta_J = 1.0$. (f) Calculated displacement of the droplet. (g) Phase diagram for the direction of the droplet motion.

This explains the experimentally observed motions of pair W or PG droplets [7] which have not been explained so far.

For a pair of droplets made of different pure liquids, evaporation rate will not be affected ($\partial J/\partial x \simeq 0$), but the surface tension will be changed locally due to the condensation of the vapor of other droplets. Since the surface tension of a liquid usually increases when vapor of other liquid having higher surface tension condenses, the droplet moves towards the droplet having higher surface tension. Similarly, the droplet having higher surface tension moves away from the droplet having lower surface tension. Thus the lower surface tension droplet chases larger surface tension droplet.

When the droplets are made of solutions, both effects of $\partial J/\partial x$ and $\partial \gamma/\partial x$ become impor-
FIG. 3. (a) An unaddressed problem: will a droplet with asymmetric initial shape move to the right or left? (b) Calculated evolution of the profile of the droplet interface between the liquid and vapor, $h(x, y = 0, t)/H_0$, for $\alpha(0) = -0.25$, $J(t) = 0$ and $\beta_S = 0$. (c) Displacement of the center of the droplet and the relaxation of the shape deformation shown in (b). Here the time is in the units of $\tau_{re}$ (the characteristic relaxation time for a deformed droplet, defined by $\tau_{re} = \eta V_0^{1/3}/\gamma_0 \theta_e^3$, where $\theta_e$ is the equilibrium contact angle). (d) Phase diagram for the direction of motion of deformable droplet in $(\beta_S, \beta_J)$ space. All parameters are the same as in Fig. 2(g), but the droplet is deformable. (e) Comparison of $\Delta x_c/R_0$ between deformable and undeformable droplets for $\beta_J = 0.2$ and $\beta_S = -0.1$. (f) Deformation parameter $\alpha(t)$ of the deformable droplet for the situation shown in (e) is plotted against $t$.

To study the direction of the droplet motion, we solved the time evolution equations obtained by the Onsager principle, and the results are shown in Fig. 2c-e. Here $\partial \gamma/\partial x$ and $\partial J/\partial x$ are assumed to be constant, and are represented by dimensionless quantities $\beta_S$ and $\beta_J$ which are defined by $\beta_S = \partial \gamma/\gamma_0 \partial x$ and $\beta_J = \tau_{ev} \partial J/\partial x$, where $\tau_{ev}$ is the characteristic evaporation time defined by $\tau_{ev} = V_0/|\dot{V}_0|$ ($V_0$ and $R_0$ are the initial size and radius of the droplet).

Figure 2f shows the evolution of the displacement of the droplet $\Delta x_c = x_c(t) - x_c(0)$ for the three cases of (c), (d) and (e). It is seen that when the mobile droplet is attracted to the fixed droplet, the speed accelerates. This is consistent with the experimental results [7].

Figure 2g shows the phase diagram for the direction of motion in the parameter space...
of \((\beta_s, \beta_f)\). Since the velocity \(\dot{x}_c\) changes in time, we define the direction of the droplet motion according to the final moving displacement \(\Delta x_f\): Attraction is for \(\Delta x_f < -0.001R_0\), Neutral is for \(-0.001R_0 \leq \Delta x_f \leq 0.001R_0\), and Repulsion is for \(\Delta x_f > 0.001R_0\).

We have discussed droplets which keep parabolic shape during evaporation [i.e., \(\alpha(t)\) is assumed to be zero]. We now consider droplets that is deformable [i.e., \(\alpha(t)\) can be non-zero].

We first consider a problem how a droplet that is initially deformed as shown by the solid black line in Fig. 3a [i.e., \(\alpha(0) < 0\)] will move as the shape relaxes to the equilibrium one. This problem is non-trivial. If we focus on the force acting on the contact line, the excess force acting on the left contact line \(\gamma_{SV} - \gamma_{SL} - \gamma \cos \theta_L\) (\(\gamma_{SV}\) and \(\gamma_{SL}\) are the substrate/vapor and substrate/liquid surface tension) is larger than the force acting on the right. Hence the droplet is expected to move to the left [11]. On the other hand, the gradient of the pressure difference in the droplet produces a capillary flow from left to right [12]. These two forces acts in opposite direction. To our knowledge, no existing theory predicts the direction of the droplet motion in this situation.

We can answer this question by Onsager principle, which gives the following time evolution equations when the effects of shape deformation, surface tension gradient and evaporation rate gradient are included (see the Supplemental Material)

\[
\dot{x}_c = \frac{R \theta^3}{3 \eta C} \frac{\partial \gamma}{\partial x} - \frac{R \partial J}{\theta} \frac{\partial \gamma}{\partial x} + \frac{\gamma_0 R \theta^3}{3 \eta C} \alpha, \quad (9)
\]

\[
\dot{\alpha} = \frac{2 \theta}{\eta RC} \left( 1 - \frac{4 \theta^2}{3} \right) \frac{\partial \gamma}{\partial x} - \frac{8 \gamma_0 \theta^3}{3 \eta RC} \alpha. \quad (10)
\]

Figure 3b and c show an example of the solution of the above equation for the case of no evaporation \([J(t) = 0]\) and no Marangoni effect \((\partial \gamma/\partial x = 0)\) with an initially asymmetric shape \([\alpha(0) = -0.25]\). It is seen that the droplet quickly relaxes to its equilibrium shape and stops. As the shape relaxation takes place, the droplet moves from small contact angle side to the large contact angle side: the direction opposite to the flow induced by the Laplace pressure. Again, this result can be explained in terms of the minimum-energy dissipation principle: if the contact line is pinned, the fluid flows from the large contact angle side to the small contact angle side; but if the contact line is mobile, the center of the droplet move from the small contact angle side to the large contact angle side in order to reduce the energy dissipation associated with the fluid flow.

Figure 3d shows a phase diagram of the direction of the droplet motion in \((\beta_s, \beta_f)\) plane for deformable droplet. Compared with Fig. 2g, it is seen that the area of attraction becomes
larger for deformable droplet than for undeformable droplet: the Marangoni effect on the motion becomes weaker.

Figure 3e shows the trajectory of $\Delta_{xc}$ for both deformable and undeformable droplets. The undeformable droplet moves faster than the deformable droplet. Figure 3f is the evolution of $\alpha(t)$, which clearly indicates that the motion is accompanied by the shape deformation. Although a negative $\alpha$ enhances the approaching velocity of droplets, the velocity of deformable droplet is smaller than the undeformable one.

This can be understood as follows. Equation (10) indicates that a part of the free energy is used to deform the shape of a droplet, while it is fully used to move the droplet that is undeformable (or more rigid). Therefore, for deformable droplets, the migration velocity becomes smaller, and larger value of $\beta_S$ is needed to change the direction of the droplet motion.

The theory presented so far can be used to simulate the motion of many droplets. Figure 4 shows the motion of two droplets made of different kinds of liquids placed on an inert solid substrate. The gradients of the evaporation rate and surface tension of the droplets are assumed to be constant and are set as in the caption. This parameter set gives the positive migration velocity for both droplet with the left larger than the right, and causes a chasing motion.

In the present theory, we have assumed that the surface property of the substrate is unaffected by vapor and remains uniform. If a gradient is created for the surface property, an additional force is created which drives the droplet from high surface energy region to low surface energy region. This problem has been theoretically discussed by Brochard et al [18] and Xu et al [19] and they predicted

$$\dot{x}_c = \alpha_v \frac{H}{\eta C} \frac{\partial \gamma_{SL}}{\partial x},$$

(11)

where $\alpha_v$ is a positive constant that depends on the shape of the droplet. The same equation can be derived from the Onsager principle (see Supplemental Material). Equation (11) can be added to the evolution Eq. (9) if there is a gradient in the surface energy of the substrate.

To summarize, we have presented a theory for the motion of evaporating droplets on an inert substrate that remains uniform. The theory explains that (a) in a same pure liquid droplet pair, they always attract each other, (b) in a different pure liquid pair, the lower surface tension droplet chases larger surface tension droplet, and (c) in a solution
FIG. 4. Simulation of the motion of two evaporating droplets. Parameters used in this calculation are: $\beta_L^S = 3.5$, $\beta_R^S = 3.0$, $\beta_L^J = -1.0$ and $\beta_R^J = 1.0$. Chasing is observed.

droplet pair, they attract, repel or chase each other depending on the surface tension and the evaporation rate. The theory can also be used to simulate the complex motion of many droplets evaporating on a substrate.

We thank T. A. Witten and D. Andelman for useful discussions. This work was supported in part by Grant No. 21404003 and 21434001 of the National Natural Science Foundation of China (NSFC), and the joint NSFC-ISF Research Program, jointly funded by the NSFC under Grant No. 51561145002 and the Israel Science Foundation (ISF) under Grant No. 885/15.

[1] J. G. Leidenfrost, *De aquae communis nonnullis qualitatibus tractatus* (Duisburg, 1756); transl. C. Wares, *Int. J. Heat Mass Transfer* **9**, 1153 (1966).
[2] D. H. Bangham and Z. Saweris, *Trans. Faraday Soc.* **34**, 554 (1938).
[3] R. L. Cottington, C. M. Murphy, and C. R. Singleterry, *Adv. Chem.* **43**, 341 (1964).
[4] P. Carles and A. M. Cazabat, Colloids Surf. 41, 97 (1989).
[5] P. Bahadur, P. S. Yadav, K. Chaurasia, A. Leh, and R. Tadmor, J. Colloid Interf. Sci. 332, 455 (2009).
[6] M. Sellier, V. Nock, C. Gaubert, and C. Verdier, Eur. Phys. J. Special Topics 219, 131 (2013).
[7] N. J. Cira, A. Benusiglio, and M. Prakash, Nature 519, 446 (2015).
[8] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, and T. A. Witten, Phys. Rev. E 62, 756 (2000).
[9] M. Kobayashi, M. Makino, T. Okuzono, and M. Doi, J. Phys. Soc. Jpn. 79, 044802 (2010).
[10] T. K. Pradhan and P. K. Panigrahi, Colloids Surf. A 482, 562 (2015).
[11] S. Daniel, M. K. Chaudhury, and J. C. Chen, Science 291, 633 (2001).
[12] D. T. Wasan, A. D. Nikolov, and H. Brenner, Science 291, 605 (2001).
[13] M. K. Chaudhury and G. M. Whitesides, Science 256, 1539 (1992).
[14] J. B. Brzoska, F. Brochard, and F. Rondelez, Langmuir 9, 2220 (1993).
[15] B. S. Gallardo, V. K. Gupta, F. D. Eagerton, L. I. Jong, V. S. Craig, R. R. Shah, and N. L. Abbott, Science 283, 57 (1990).
[16] K. Ichimura, S. K. Oh, and M. Nakagawa, Science 288, 1624 (2000).
[17] R. W. Style, et al. Proc. Natl Acad. Sci. USA 110, 12541 (2013).
[18] F. Brochard, Langmuir 5, 432 (1989).
[19] X. P. Xu and T. Z. Qian, Phys. Rev. E 85, 051601 (2012).
[20] M. Doi, Soft Matter Physics (Oxford University Press, New York, 2013).
[21] M. Doi, Chin. Phys. B 24, 020505 (2015).
[22] X. M. Xu, Y. N. Di, and M. Doi, Phys. Fluids 28, 087101 (2016).
[23] X. K. Man and M. Doi, Phys. Rev. Lett. 116, 066101 (2016).