

Contact Line Dynamics in the Late-Stage Coalescence of Diethylene Glycol Drops[†]

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We investigated the contact line dynamics of a composite drop formed as a result of the coalescence during the condensation of two diethylene glycol (DEG) drops at $-4\text{ }^{\circ}\text{C}$ on a silicon surface. The composite drop relaxes exponentially toward equilibrium with a typical relaxation time, t_c , which depends on the equilibrium radius, R , of the composite drop. The value of t_c is found to be in the range of 10–100 s for $R \approx 1\text{--}4\text{ }\mu\text{m}$. The relaxation dynamics is found to be larger by 6 orders of magnitude than that predicted by bulk hydrodynamics because of high dissipation in the contact line vicinity. Similar to low viscous liquids (water), this high dissipation can be attributed to an Arrhenius factor resulting from the phase change in the contact line vicinity and to the influence of surface defects that pin the contact line.

1. Introduction

Coalescence is a key phenomenon in breath figures or dew formation,^{1,2} early stages of thin film growth,^{3,4} phase separation of two-phase flow,^{5,6} microfluidics,⁷ and so forth. While it has been the subject of fundamental research^{8–10} since long ago, the details of coalescence dynamics are not yet clearly understood. In the case of the coalescence of freely suspended drops, the knowledge of the liquid viscosity and surface tension is sufficient to describe the kinetics of the coalescence, whereas, for sessile drops coalescence, the contact line motion strongly influences the coalescence kinetics. The coalescence phenomenon is basically a two-stage process: (i) the bridge formation and (ii) the relaxation (contact line motion of the composite drop formed as a result of the coalescence). At early times, a bridge (neck) is formed between two drops. The bridge (neck) radius grows as $r_b \propto t^{1/2}$.^{11–16} At late times, the composite drop relaxes exponentially toward a spherical shape where the contact line motion plays a key role. The relaxation of a composite drop for small capillary numbers ($\text{Ca} < 10^{-5}$) has been studied experimentally for low viscosity liquids such as water.^{17,18} The relaxation time appeared to be nearly 10^7 times larger than bulk capillary relaxation, as an effect of the contact line dynamics.

The theories of contact line dynamics^{19–26} result in a general expression for contact line velocity v_n in a direction normal to the contact line:

$$v_n = \frac{\sigma}{\xi} (\cos \theta_{\text{eq}} - \cos \theta) \quad (1)$$

where θ is the dynamic contact angle, θ_{eq} is the equilibrium contact angle, σ is the surface tension, and ξ is a model-dependent parameter called the “*contact line dissipation coefficient*”. Another aspect of these theories is that they predict a very large ξ value so that $K = \eta/\xi$, where η is the viscosity, is much smaller than unity. For the contact line motion of receding

water drops on a silanized glass surface, Andrieu et al.¹⁷ measured $K \approx 10^{-6} - 10^{-7}$. Recently, these results were confirmed and extended by Narhe et al.¹⁸ for the contact line motion of a composite water drop on silicon and polyethylene surfaces. In the theoretical study of the relaxation of a contact line in the presence of random defects, Nikolayev¹⁹ observed near the depinning threshold a nonlinear behavior of the mean line velocity $\langle v_n(\cos \theta) \rangle$ ($\langle \rangle$ means an average on the contact line). As a consequence, the effective dissipation coefficient that results can become larger than ξ .

The main results obtained on low viscous fluids are the following:¹⁸

1. The contact line dynamics during coalescence can be markedly affected by initial conditions. For instance, if the coalescence is induced by syringe deposition, the composite drop surface shows strong oscillations that are not observed in the coalescence induced by condensation. Each oscillation pulls the contact line and thus accelerates the motion.

2. The coalescence of water sessile drops imposed by condensation growth shows extremely small values ($K \approx 2.5 \times 10^{-6}$) for coalescence induced by condensation. The contact line dissipation makes the relaxation rate 5–6 orders of magnitude smaller compared to that of the bulk dissipation.

3. The relaxation rate was seen to increase with contact angle, leading to angle variation, which is in reasonable agreement with the theory.^{27,28}

The purpose of the present work is to study the contact line dynamics of a liquid that is much more viscous, but is still composed of small molecules. For this purpose, we considered diethylene glycol (DEG), $\text{C}_4\text{H}_{10}\text{O}_3$, at low temperatures ($-4\text{ }^{\circ}\text{C}$). We studied the contact line dynamics of a composite drop formed after the coalescence of two DEG drops during condensation. We investigated the late stages of coalescence to check whether in a viscous fluid (the viscosity of which is 160 times greater than that of water) the contact line dynamics still dominates the process in the late stages of coalescence.

2. Experimental Section

For this study, silicon wafers are used as substrates. The coalescence of two DEG drops is studied in a condensation

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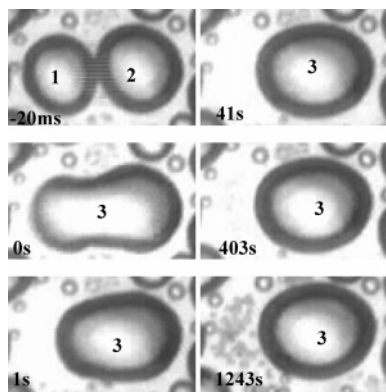


Figure 1. Optical microscope images of the coalescence process of two DEG drops on a silicon surface that was kept at $-4\text{ }^{\circ}\text{C}$ in a condensation chamber. The size of each image is $40 \times 25\text{ }\mu\text{m}$.

chamber, where droplets grow by condensation and coalesce when they touch each other. We will use the DEG parameters at $-4\text{ }^{\circ}\text{C}$ ^{29,30} (surface tension $\sigma = 47\text{ mN/m}$, dynamic viscosity $\eta = 0.161\text{ Pa}\cdot\text{s}$, kinematic viscosity $\nu = 1.425 \times 10^{-4}\text{ m}^2\text{ s}^{-1}$, and density $\rho = 1.130\text{ g cm}^{-3}$).

2.1. Chamber Experiments. In condensation experiments, a small clean piece of silicon substrate ($1 \times 1\text{ cm}^2$) is fixed on a thick electrolytic copper plate by a thin film of DEG in order to have good thermal contact with the copper plate. The condensation chamber consists of a Peltier-element thermostat enclosed in a Plexiglas box. The surface temperature can be adjusted above, equal to, or below the dew temperature (T_D). The substrate is cooled from the room temperature ($T_R \approx 23\text{ }^{\circ}\text{C}$) to the desired temperature T_s , which is kept in this series of experiments at $T_s \approx -4\text{ }^{\circ}\text{C} = T_R - 27\text{ K}$. The substrate temperature is measured by a K-type thermocouple placed close to the substrate. The chamber is filled with pure N_2 gas saturated with DEG at room temperature. To avoid dust deposition and to saturate the gas, N_2 is bubbled in pure DEG. The gas flow rate is controlled with a flow meter and kept fixed at 0.6 L min^{-1} . The growth and subsequent coalescence of the drops (see Figure 1) are observed with a high-resolution black and white CCD camera (COHU, 4910 series, 50 frames/s) attached to an optical microscope (Leica, DMRXE, resolution $\approx 0.3\text{ }\mu\text{m}$) and recorded on a video recorder. The video images are then analyzed by image analysis software (Image Tool).

2.2. Surface Properties. The contact angle of DEG on silicon substrate is measured by the well-known sessile drop method. A small drop of $\sim 1\text{ }\mu\text{L}$ is deposited on the substrate by means of a microliter syringe and visualized using a CCD camera with a macro lens. The static receding contact angle (θ_r) and advancing contact angle (θ_a) are measured by removing/adding a small amount of DEG from/to the drop with a microsyringe. We introduce the “equilibrium” value of the contact angle, $\theta_{eq} = (\theta_a + \theta_r)/2 = 30 \pm 2^{\circ}$. The values of θ_a and θ_r for silicon are $\theta_a = 35 \pm 2^{\circ}$ and $\theta_r = 25 \pm 2^{\circ}$.

3. Results and Discussion

The coalescence process is characterized by three time stages:^{17,18}

3.1. Formation of a Liquid Bridge. The formation of a liquid bridge between two drops of radii R_1 and R_2 and the subsequent formation of a convex composite drop (between the time moments $t = -20\text{ ms}$ and 0 s in Figure 1) takes less than 20 ms . The drop shape can be characterized by the large axis $2R_y$, measured in the direction of maximum elongation, and the small axis $2R_x$, measured in the perpendicular direction. R_y and R_x

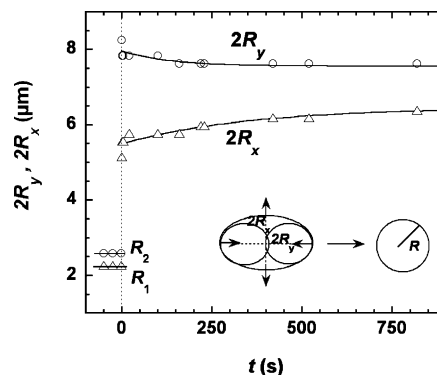


Figure 2. Typical time evolution of the large axis $2R_y$ and small axis $2R_x$ of a composite DEG drop in a condensation chamber. R_1 and R_2 are the radii of the two drops before coalescence.

are larger and smaller drop radii, respectively (see Figure 2). The contact line dynamics is characterized by a quick increase of R_x due to the advancing motion in the “bottleneck” region of the composite drop where a strong negative surface curvature exists. R_y remains practically unchanged because the contact line is pinned.

3.2. Decrease in the Larger Radius. The larger radius R_y decreases with time, and the smaller radius R_x increases such that the drop approaches the shape of a spherical cap (Figure 2).

3.3. Slow Growth of the Composite Drop. The slow growth of the composite drop occurs by condensation.

The composite drop finally becomes hemispherical with the equilibrium radius R . The dynamics is very slow, and the complete relaxation takes a very long time ($\approx 1\text{ h}$ for a $10\text{ }\mu\text{m}$ drop). The relaxation velocity is proportional to the restoring force $F_y = 2\pi R_y \sigma_{lv} (\cos \theta - \cos \theta_{eq})$,²³ which is defined by the variation in the drop surface energy (see Nikolayev and Beysens²⁷).

Figure 2 shows the time evolution of the large axis $2R_y$ and the small axis $2R_x$ of the composite drop. R_1 and R_2 are the radii of the two drops before coalescence.

From Figure 2 the relaxation time t_c can be obtained by fitting the relaxation data by an equation of the form

$$R_{x,y}(t) = R_0 \exp\left[\frac{-(t - t_0)}{t_c}\right] + R + A(t - t_0) \quad (2)$$

The first term corresponds to the relaxation of the composite drop, which is dominating in regime 2, and the third term approximately describes the slow growth due to condensation in regime 3. The time at which coalescence begins is t_0 . Its experimental value is imposed in the fit. R_0 , R , A , and t_c are the fitting parameters. Figure 3 shows the relaxation time t_c versus the equilibrium radius R . One can deduce that the relaxation time t_c follows a linear variation with the final equilibrium radius R of the drop, similar to what was found for water drops.^{17,18}

$$t_c = \left(\frac{1}{U^*}\right)R \quad (3)$$

Here the velocity U^* characterizes the contact line relaxation rate. This velocity is not to be confused with the contact line speed, which obviously varies during the relaxation process. The fit gives $U^* = (4.5 \pm 0.5) \times 10^{-8}\text{ m s}^{-1}$ (error: one standard deviation). Since DEG has a low saturation vapor pressure (at $20\text{ }^{\circ}\text{C}$, it is lower than 0.01 mm Hg), the drops grow very slowly by condensation. It is therefore difficult to

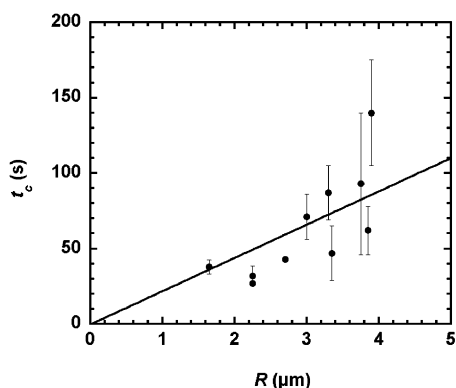


Figure 3. The relaxation time t_c versus the equilibrium drop radius R . The line is the best fit to eq 3.

produce a very large drop of DEG in a reasonable experimental time (on the order of a day).

According to Nikolayev and Beysens,²⁷ t_c should vary with θ as

$$t_c = \frac{1}{K} \frac{\eta}{\sigma} \phi(\theta) R \quad (4)$$

This defines U^* as

$$U^* = K \frac{\sigma}{\eta} \frac{1}{\phi(\theta)} \quad (5)$$

with

$$\phi(\theta) = \frac{45}{(108 + 41 \cos \theta + 14 \cos^2 \theta + 17 \cos^3 \theta)(1 - \cos \theta)} \quad (6)$$

Using eqs 3, 5, and 6 for $\theta = 30^\circ$ ($\phi = 3.8$) and $U = \sigma/\eta = 0.29 \text{ m s}^{-1}$, we obtain $K = 5.9 \times 10^{-7}$ for the DEG drop. Such small K values clearly show that the dynamics of viscous sessile drops in the regime of partial wetting is limited by the dissipation at the region of the drop close to the contact line. According to Pomeau,²⁶ the delay is due to the Arrhenius kinetic factor resulting from a liquid–vapor phase change in the vicinity of the contact line. The model results in a large relaxation time where $K_P \sim \exp(L/RT)$, with L being the molar latent heat of vaporization, R being the gas constant, and T being the temperature. For DEG, $L \approx 52.3 \text{ kJ/mol}$,²⁹ corresponding to $K_P \approx 10^{-10}$. For water, the same calculation with $L \approx 44 \text{ kJ/mol}$ leads to $K_P \approx 2 \times 10^{-8}$. Although the discrepancies with the experimental values are large because of the exponential factor, for both liquids they lead to an excess of 2–3 orders of magnitude compared to the experimental values. It is likely that the surface heterogeneities also play a role in (i) slowing down the contact line motion near the pinning threshold, as outlined by Nikolayev¹⁹, and (ii) pinning the contact line in an early

metastable state, thus giving an effective relaxation time smaller than that which a theory without surface defects might predict.

Conclusion

The experiments show that, for viscous sessile DEG drops during coalescence induced by condensation, the viscous relaxation time is 6–7 orders of magnitude larger than bulk hydrodynamic relaxation time. This extremely small value shows that, at the late stages of coalescence, the contact line dynamics still dominate the process.

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References and Notes

- (1) Beysens, D.; Knobler, C. M. *Phys. Rev. Lett.* **1986**, *57*, 1433.
- (2) Muselli, M.; Beysens, D.; Marcillat, J.; Milimouk, I.; Nilsson, T.; Louche, A. *Atmos. Res.* **2002**, *64*, 297.
- (3) Narhe, R. D.; Khandkar, M. D.; Adhi, K. P.; Limaye, A. V.; Sinkar, S. R.; Ogale, S. B. *Phys. Rev. Lett.* **2001**, *86*, 1570.
- (4) Beysens, D.; Knobler, C. M.; Schaffar, H. *Phys. Rev. B* **1990**, *41*, 9814.
- (5) Tanaka, H. *Phys. Rev. Lett.* **1994**, *72*, 1702.
- (6) Nikolayev, V. S.; Beysens, D.; Guenoun, P. *Phys. Rev. Lett.* **1996**, *76*, 3144.
- (7) Gau, H.; Herminghaus, S.; Lenz, P.; Lipowsky, R. *Science* **1999**, *283*, 46.
- (8) Thomson, J.; Newall, H. *Proc. R. Soc. London* **1885**, *39*, 417.
- (9) Rayleigh, L. *Proc. R. Soc. London* **1879**, *28*, 406.
- (10) Reynolds, O. *Philos. Trans. R. Soc. London* **1886**, *177*, 157.
- (11) Eggers, J.; Lister, J. R.; Stone, H. J. *Fluid Mech.* **1999**, *401*, 293.
- (12) Duchemin, L.; Eggers, J.; Josserand, C. *J. Fluid Mech.* **2003**, *487*, 167.
- (13) Menchaca-Rocha, A.; Martnez-Dávalos, A.; Nùñez, R. Popinet, S.; Zaleski, S. *Phys. Rev. E* **2001**, *63*, 046309.
- (14) Wu, M.; Cubaud, T.; Ho, C. M. *Phys. Fluids* **2004**, *16*, L51.
- (15) Thoroddsen, S. T.; Takehara, K.; Etoh, T. G. *J. Fluid Mech.* **2005**, *527*, 85.
- (16) Narhe, R. D.; Beysens, D. A. Unpublished work, 2004.
- (17) Andrieu, C.; Beysens, D. A.; Nikolayev, V. S.; Pomeau, Y. *J. Fluid Mech.* **2002**, *453*, 427.
- (18) Narhe, R.; Beysens, D.; Nikolayev, V. S. *Langmuir* **2004**, *20*, 1213.
- (19) Nikolayev, V. S. *J. Phys. Condens. Matter* **2005**, *17*, 2111.
- (20) De Gennes, P. G. *Rev. Mod. Phys.* **1985**, *57*, 827.
- (21) Voué, M.; Valignat, M. P.; Oshanin, G.; Cazabat, A. M.; de Coninck, J. *Langmuir* **1998**, *14*, 5951.
- (22) Blake, T. D.; Decamps, C.; De Coninck, J.; de Ruijter, M.; Voué, M. *Colloids Surf., A* **1999**, *154*, 5.
- (23) de Ruijter, M. J.; De Coninck, J.; Oshanin, G. *Langmuir* **1999**, *15* (5), 2209.
- (24) de Ruijter, M. J.; De Coninck, J.; Blake, T. D.; Clarke, A.; Rainkin, A. *Langmuir* **1997**, *13*, 7293.
- (25) Blake, T. D.; Haynes, J. M. *J. Colloid Interface Sci.* **1969**, *30*, 421.
- (26) Pomeau, Y. *C. R. Acad. Sci., Ser. IIb: Mec., Phys., Chim., Astron.* **2000**, *238*, 411.
- (27) Nikolayev, V. S.; Beysens, D. A. *Phys. Rev. E* **2002**, *65*, 46135.
- (28) Iliev, S.; Pesheva, N.; Nikolayev, V. S. *Phys. Rev. E* **2005**, *72*, 011606.
- (29) The values of σ and η for DEG at -4°C are obtained from the linear extrapolation of the temperature–surface tension graph and the exponential extrapolation of the temperature–viscosity graph of DEG data for the temperature range $25\text{--}100^\circ\text{C}$. The data are taken from the CRC manual.
- (30) Zen Backpacking Stoves Home Page. <http://zenstoves.net/CHRIS/DEG.pdf> (accessed Oct 2005).