Moving Mercury Drop by Chemical Reaction

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1. Beating of a Mercury Drop

Mercury, or quicksilver, is the only material among the metals that is in the liquid state under room temperature. The surface tension of that material is 475 [dyne/cm] at 20°C, which is quite large compared with that of the water (72.75 [dyne/cm]). In general, the effect of the gravity force becomes smaller for smaller drop compared with the effect of the surface tension, which explains why the shape of a small mercury drop is nearly spherical, and rolls down over a slightly tilted plane.

Spontaneous beating of a mercury drop in sulfuric acid H_2SO_4 associated with potassium permanganate $KMnO_4$ or associated with potassium dichromate $K_2Cr_2O_7$ has been widely known (Freundlich, 1930; Alyea and Dutton, 1960; Keiser *et al.*, 1979; Kai, 1986; Avnir, 1989), and its mechanism is attributed to an electro-capillary phenomenon, in which surface tension between two kinds of fluid varies by applying a potential difference and charges (Lippmann, 1873; Bard and Faulkner, 1980). Similarly, in "beating mercury heart" system, the potential difference between the mercury and the tungsten or iron tip in the presence of an acidic solution as well as a corroding electrode is essential to electron transfer processes, which changes the magnitude of surface tension. By an appropriate positioning of the electrode tip with respect to the mercury drop, a kind of electric circuit is switched on and off, which leads to a mechanical oscillation. Sometimes the formation of film on the surface of the mercury seems to be involved. The center of gravity of the drop, however, remains fixed in these cases.

2. Autonomous Translational Motion of a Mercury Drop

When a mercury drop is placed in a petri dish filled with HNO_3 and $K_2Cr_2O_7$ solutions, it reveals autonomous translational motion in an otherwise quiescent fluid (Watanabe and Kutsumi, 1992; Watanabe *et al.*, 1994). Typical autonomous translation is observed in a mercury drop of about 2–3 mm diameter placed in a *uniform* solution of about 1.0 [mol/dm^3] HNO_3 with 0.15 g (5.1×10^{-4} [mol]) of $K_2Cr_2O_7$. The speed of the droplet has an order of a few mm/s. A reddish substance containing very fine particles (considered to be a mercurous chromate Hg_2CrO_4) is produced at the surface of the mercury drop, which encloses the drop and diffuses into the bulk fluid.

With some initial disturbance, the latter distribution becomes non-uniform, which initiates the translational motion of the drop due to the unbalance of surface tension. Once this happens, the reddish substance is swept along to the rear side of the drop and is left behind, which shows the orbit of the drop. The typical shape of the translating mercury drop resembles that of a *croissant* with broad convex surface perpendicular to the direction of motion. Although the direction and magnitude of the movement of the droplet change irregularly, the average speed is almost independent of its size. If the initial mercury drop is as large as 1 cm, however, that globule is stretched and broken into smaller droplets, each of which moves as described above. These droplets translate almost independently in random directions, but the collisions of the droplets with each other seem avoided as if they knew the position of the other (see Fig. 1).

3. Motive Force of the Mercury Drop

The front surface of the drop in translational motion is always exposed to a "fresh solution", and chemical reaction is repeated. Such a constant exposure of its front surface to a solution with rich chemicals will keep the fore-aft asymmetry of the surface tension, which is considered to be the origin of the mechanical motion of the drop.

Let us assume that the mercury drop is spherical and the surface tension distribution $\gamma(\theta)$ is given in terms of the spherical coordinate system by

$$\gamma(\theta) = \gamma_0 - \Gamma\cos\theta,$$

where θ is the polar angle with its axis in the direction of motion, and γ_0 and Γ are positive constants. Assuming the Stokes approximation, the fluid mechanical drag force on the drop moving at a constant speed U is calculated, which is balanced with the driving force due to nonuniform surface tension. Then, after some mathematical manipulation, we

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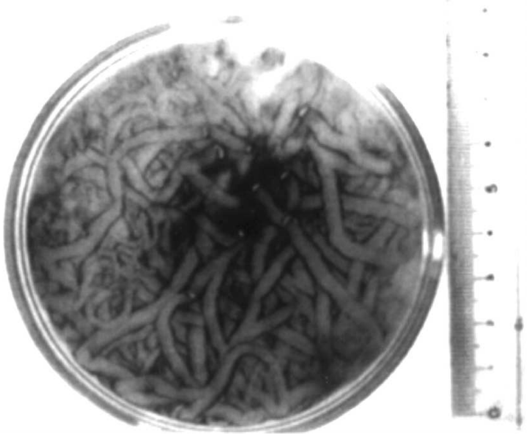

Fig. 1. Traces of several mercury droplets after sufficient time.

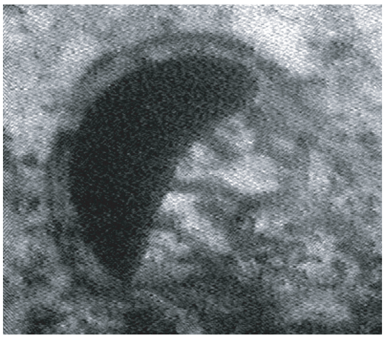

Fig. 2. Typical planform of a mercury drop in translation. Direction of motion is left-upward in the photograph.

have

$$U = \frac{2\Gamma}{3(2\mu + 3\mu^*)},$$

where μ and μ^* is the viscosity of the solution and mercury, respectively (Levich and Krylov, 1969; Watanabe *et al.*, 1994). Here, the frictional force between the droplet and the bottom wall has been neglected because of the presence of the liquid film between them, as well as the induced flow inside the droplet.

4. Shape of the Mercury Drop in Translational Motion

Figure 2 is an example of the mercury drop in steady translational motion. Although the planform looks crescent with its convex side toward the moving direction, the 3D figure resembles a spindle with its axis bent forward, like a *croissant*. The drop sometimes shows an ellipsoidal form during unsteady motions (see Fig. 3(ii)).

A simple analysis on the basis of the Stokes approximation, taking into account of the non-uniform distribution of chemically reacting material, explains the shape of the droplet (Watanabe *et al.*, 1994). Here, the viscous shear stresses and the dynamic pressure associated with translational motion are estimated to be much smaller than the surface tension, so that the equilibrium shape is realized by the balance of pressures due to the latter:

$$\gamma_f \left(\frac{1}{R_f} + \frac{1}{R_0} \right) = \gamma_b \left(\frac{1}{R_b} + \frac{1}{R_0}, \right)$$

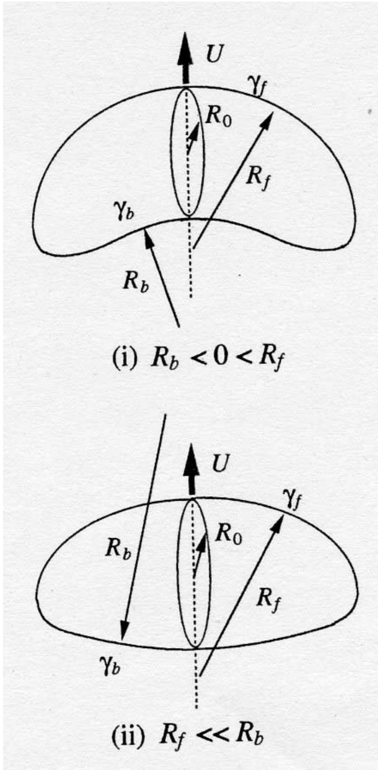

Fig. 3. Illustrative figures of the equilibrium shape of a drop under non-uniform distribution of surface tension.

where R_f, R_0 and R_b, R_0 are the radii of the drop in the front side and the rear side, respectively. The surface tension coefficients in the front side γ_f and in the rear side γ_b can be different depending on the extent of chemical reaction. In the constantly moving phase, the chemical reaction proceeds mainly in the front side, which results in $\gamma_f < \gamma_b$, and hence

$$\frac{\gamma_b}{R_b} < \frac{\gamma_f}{R_f}.$$

This relation is satisfied either by (i) $R_b < 0 < R_f$ or (ii) $R_f \ll R_b$ (if γ_f and γ_b are the same order due to slow chemical reaction), which correspond to case (i) and case (ii) of Fig. 3, respectively.

5. Change of Direction of the Mercury Drop in Translational Motion

As shown in Fig. 1, each droplet pushes aside the reddish substance that was produced by the chemical reactions. Typically, the traces are nearly straight lines, accompanied by local change of directions immediately before the droplet reaches the container wall or immediately before it touches another drop.

The motions of the mercury droplets look like those of living creatures that avoid collisions to each other, with the exception of orientation of the bodies, i.e., the former moves broad-side on in contrast to the latter. Whenever the “crescent” becomes tilted with respect to the moving direction, the unbalance of surface tension recovers the right-left symmetry and the broad-side on motion is maintained.

The deceleration of the two approaching droplets, or the one toward the container wall, will be caused by the flattening of the front side and the reduction of "fresh solution" in the forward regions. Resulting decrease of the net force ultimately terminates the forward motion, by which the force in the perpendicular directions becomes dominant, leading to the turning motion of the droplet.

6. Oscillatory Translational Motion and the Polygonal Shape Oscillation of the Mercury Drop in the Solution with Density Gradient

Mercury droplet moves toward larger density of potassium dichromate $K_2Cr_2O_7$ in HNO_3 solution. The resulting reddish substance that encloses the drop, however, reduces the translational motion in this direction, which ceases further forward motion. At this moment, the density of the reddish substance is smaller in the rear side, which induces translational motion in the reverse direction. These processes are repeated to realize the oscillatory translational motion of the droplet. At the same time, the polygonal shape oscillation is induced, which is considered to be the characteristic vibration. The latter is also maintained by the change of surface tension due to chemical reaction (Sano *et al.*, 1995).

7. Translational Motion of a Droplet of Other Species

Another widely known example that shows the translational motion is a drop of TSAC (Trimethyl Stearyl Ammonium Chloride) in Nitrobenzen, Potassium Iodine, Iodine solution. The surface tension of this drop is not as large as that of the mercury, so that the translational motion is rather random and is accompanied by larger irregular deformation. By an appropriate control of the drop, however, well-organized motions such as translational motion and oscillatory motion, are also observed (Sumino *et al.*, 2005; Sumino and Yoshikawa, 2014).

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