Spontaneous Jumps of a Droplet

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Water droplets condensing with a nonzero contact angle on a solid substrate maintained near its melting point exhibit a very unusual behavior. Droplet growth is accompanied by rotation, translation, and hopping movements. Microscopic observations show that the substrate melts along the line of three-phase contact. An analysis of the flow rate and temperature dependence of the phenomenon indicates that droplets are set into motion by the relaxation of the substrate strain during melting.

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When a drop of liquid is placed on a solid, the resultant surface tension should cause an elastic strain in the substrate, localized at the drop perimeter (the line of three-phase contact, which we call in the following the contact line). Surprisingly, these forces have not yet been clearly evidenced [1]. Even the Young's relation itself is still questioned [2]. We report here the observation of a very curious phenomenon which shows the existence of the tensions of the perimeter of the drop: During the condensation process of drops on a solid substrate that locally melts, the release of the substrate strain is able to move the drops, which literally "jump." This phenomenon, to our knowledge, has remained unnoticed until now and could have applications for heat and mass transfer, as also during the early stages of thin-film growth. It demonstrates, in addition, that the mass transfer during condensation is mostly performed at the contact line location.

We show evidence of this phenomenon in breath figures (BF), the pattern of droplets condensing on a substrate with a nonzero contact angle. A BF is a simple experimental model which has been frequently studied recently [3]. The experimental setup is identical to that already used for BF experiments [3]. It is basically a chamber into which a constant flow (rate F) of nitrogen gas saturated with water vapor at a constant temperature T_r (typically 23.0 °C) is sent. The condensation occurs on a substrate maintained at a constant temperature T_s by means of a Peltier element. Nucleation and growth of the droplets on the solid are observed by using an optical microscope and a charge-coupled-device video camera. Subsequent analysis is performed on an image analysis system.

A droplet of radius R which does not undergo coalescence is known to grow as (see [3] and references therein for the physical arguments leading to this result)

$$R=(K\sqrt{F}\,\Delta P_{rs}\,t/T_s)^{1/3}, \quad (1)$$

where this equation expresses a growth process by condensation on the droplet. Here K is a numerical constant which depends on the geometry of the chamber, ΔP_{rs} is the difference in water saturated pressure at temperatures T_s and T_r, and t is the time measured from the start of the flow into the chamber (in this experiment the nucleation time is negligible because the nucleation is heterogeneous). The substrate used is solid cyclohexane whose temperature is maintained at T_s ranging from -1 to 6.2 °C. This temperature is close to its melting temperature at atmospheric pressure ($T_m = 6.68\,°\mathrm{C}$).

The observations are the following. When the gas flow is directed on the substrate, water droplets with a contact angle of 90° form and grow. This is similar to the BF experiment on silanized glass. The striking differences are the translation and rotation movements that these drops exhibit during their growth. These movements stop instantaneously when the flow rate is set to zero. Three different types of movements can be characterized. The most common one is the stepwise motion which is similar to Brownian motion or hopping. The drops seem to jump instantaneously (i.e., in a time lower than the video scanning time of 40 ms) from one position to another. These jumps take place in any direction on the substrate and the distance between the two positions is always of order R. Once a drop has jumped, its former position remains visible on the substrate by a perimeter print [Fig. 1(a)]. Note that it is clear in this photograph that all the regions of the substrate which are not at the drop perimeter keep the same defects before and after the jump, which means that these regions have not melted. In fact, these "jumps" are not real jumps because gravity is not relevant in the problem; the same motion is observed when the substrate is horizontal, vertical, or even upside down because the drops always keep a contact with the substrate when they move. The typical time τ between jumps is longer for larger drops. A second kind of motion that is observed involves the movement of the drops in the same direction, along a linear defect in the substrate. It is often a back and forth movement between two point defects on this line. The third type of motion is a rotation around a fixed point which always appears to be a defect in the substrate. The typical time of these two movements varies as τ defined above. When the droplets become much larger than the size of the defect, hopping motion is recovered. Therefore we interpret these latter

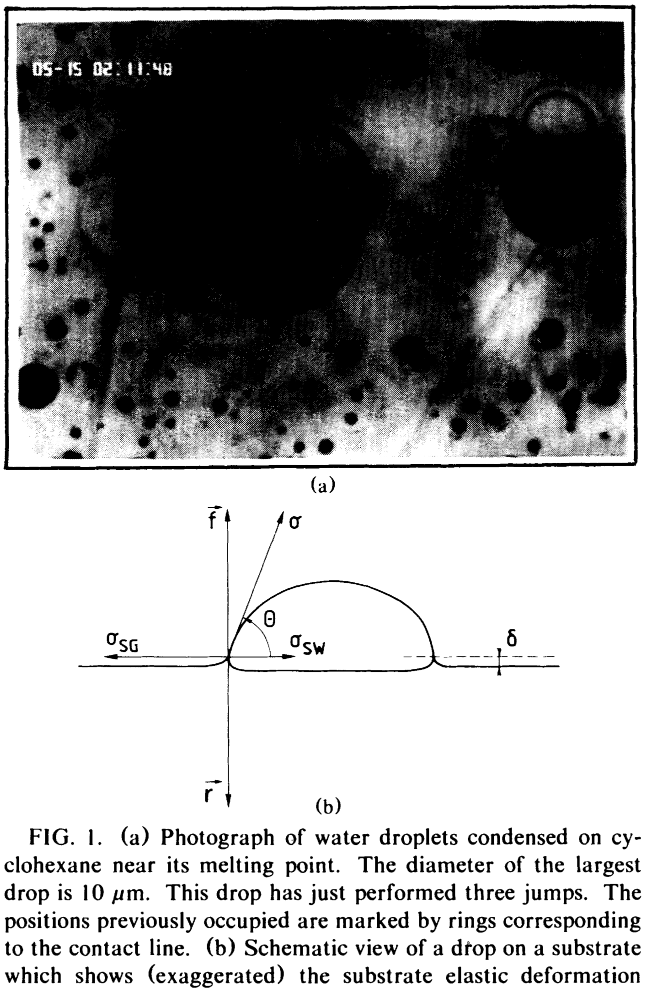

FIG. 1. (a) Photograph of water droplets condensed on cyclohexane near its melting point. The diameter of the largest drop is 10 μm. This drop has just performed three jumps. The positions previously occupied are marked by rings corresponding to the contact line. (b) Schematic view of a drop on a substrate which shows (exaggerated) the substrate elastic deformation (δ) due to the resultant surface-tension force **f**. **r** is the substrate reaction that prevents the drop from moving. σ, σ_{SG}, and σ_{SW} are the surface tensions between gas and water, gas and substrate, and substrate and water, respectively. The construction of the forces represents the Young's relation: $\sigma_{SG}-\sigma_{SW}=\sigma\cos\theta$. If the drop grows by condensation, the latent heat is able to heat and melt the substrate, which results in the releasing of the elastic constraints: The drop "jumps."

two movements (translation, rotation) as being derived from hopping movements in special situations where the droplet motion is guided by the unavoidable imperfections of the substrate. We will consider in the following only the hopping motion.

This rather surprising hopping motion cannot be explained by Marangoni effects. Such an effect would have needed a heat flux or a mass flux that is nonsymmetrical across the drop perimeter. The fact that the drop motion stops immediately when the gas flux is stopped rules out a solubility Marangoni effect. A thermal effect would have been observed in similar thermal situations where water droplets are condensed on an immiscible liquid (as paraffin oil in Ref. [3]). In fact the only motion that has been observed on liquid substrates was due to the elastic deformations of the oil interfaces. In contrast, the motion can be explained as due to the release of the substrate strains. Because of the existence of the surface tension, three forces are counterbalanced at the vapor-liquid-substrate contact line. In contrast to the situation where the substrate is a liquid, the resultant force **f** cannot be zero for a solid substrate. In this case, the solid imposes the direction of two of the three tensions [Fig. 1(b)]. As a result, there is a nonzero resultant force directed vertically at the contact line. This force is balanced by the reaction force **r** of the substrate, which prevents the drop from jumping. This leads to an elastic deformation (δ) of the substrate, and consequently to a storage of energy. The deformation is usually very small for the usual solids (with an elastic constant of order 10^9 N m^{-2}, $\delta\sim1$ Å [1]) and is often neglected. However, deformations of "soft" substrates by large drops have been reported, such as on solid paraffin slightly below its melting point [4] or on gels [5]. In our case, the latent heat of condensation of water is able to melt the substrate locally. It is clear from Fig. 1(a) that such a melting is localized along the drop contact line. Melting suppresses the substrate reaction force and the drop becomes unstable. The stored elastic energy is now used to move the drop, that remains in contact with the substrate with a film of melted solid. An upper limit of the initial acceleration γ can be estimated according to the following formula, when the resultant surface-tension force on the drop is $2\pi\sigma R$, with σ the surface tension between water and gas:

$$\gamma=3\pi\sigma R(\pi R^3\rho)^{-1}=3\sigma(\rho R^2)^{-1}. \tag{2}$$

Here ρ is the drop density. A numerical estimation gives (for water $\sigma\sim70$ cgs, $\rho\simeq1$ g cm^{-3}) an acceleration $\gamma=2\times10^8$ cm s^{-2} for droplets of radius $R=10$ μm, which gives a typical time of the order of a few μs for a jump. This explains why details of the motion of the drop cannot be observed in the video scanning time (40 ms).

These movements are discontinuous because a time (τ) is needed to heat cyclohexane up to its melting tempera-

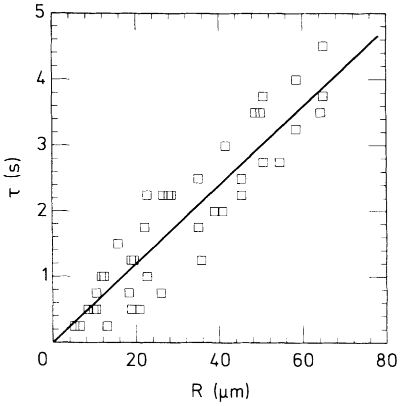

FIG. 2. Time τ between jumps vs the drop radius. ($T_s=3.4\,^\circ$C, $T_r=24.2\,^\circ$C, $F=10$ l/h.)

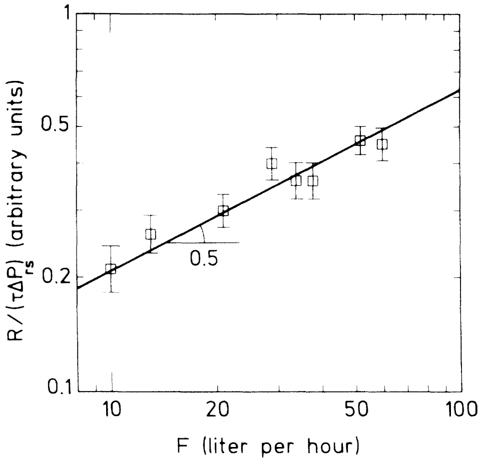

FIG. 3. Quantity $R(\Delta P_{rs}\tau)^{-1}$ vs flow rate F in a log-log scale. The slope 0.5 is indicated. ($T_s = 3.4\,°\mathrm{C}$, $T_r = 24.2\,°\mathrm{C}$.)

ture and to provide its enthalpy of melting. One can write a proportionality relation between the quantity of heat released by condensation on the drop, with a volume change of $2\pi\Delta R^3/3$, and the quantity of heat used to heat the cyclohexane up to its melting point. The volume of melted cyclohexane is proportional to R because melting occurs mainly at the perimeter of the drop. This is expressed by the equation

$$RC_p(T_m - T_s) \sim L_w \Delta R^3 , \tag{3}$$

where C_p is the specific heat of cyclohexane, and L_w the latent heat of condensation of water. The latent heat of cyclohexane has been omitted since the drop starts to move at the onset of the melting process. By making use of Eq. (1) to express the time dependence of R, one obtains

$$L_w \sqrt{F}\, \Delta P_{rs}\, \tau / T_s \sim RC_p(T_m - T_s) . \tag{4}$$

Equation (4) can be checked. First, the analysis of the video pictures enables τ and R to be determined when the temperatures T_s, T_r and the flow rate F are varied. The linear relationship between R and τ is well verified in Fig. 2. The data in Fig. 2 represent measurements on many drops with different radii. It would have been ideal to plot τ vs R for a single drop, but this is impossible: The drops are growing and moving, causing many coalescence events which prevent the same drop from being studied long enough. The flow-rate dependence is displayed in Fig. 3, where the quantity $R(\Delta P_{rs}\tau)^{-1}$ has been plotted with respect to F in a log-log plot, revealing a power law with an exponent $\frac{1}{2}$. A final test is provided by the linear dependence of $\Delta P_{rs}\tau(RT_s)^{-1}$ with respect to temperature T_s (Fig. 4). This relation is not well checked near T_m, where the entire surface of the substrate beneath the drop begins to melt. In these conditions a thin film of cyclohexane is present. The intercept, however, occurs at a temperature of the order of T_m, as expected from Eq (4).

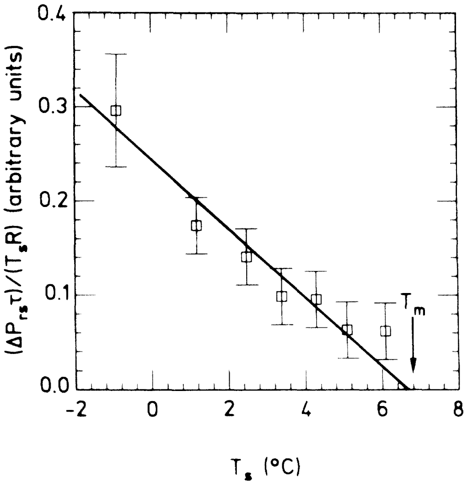

FIG. 4. Variation of $\tau\Delta P_{rs}(T_s R)^{-1}$ vs T_s ($F = 35$ l/h). The intercept of the straight line is a value close to the cyclohexane melting temperature (6.7 °C). The deviation near T_m is attributed to an increasing amount of molten substrate in the vicinity of T_m.

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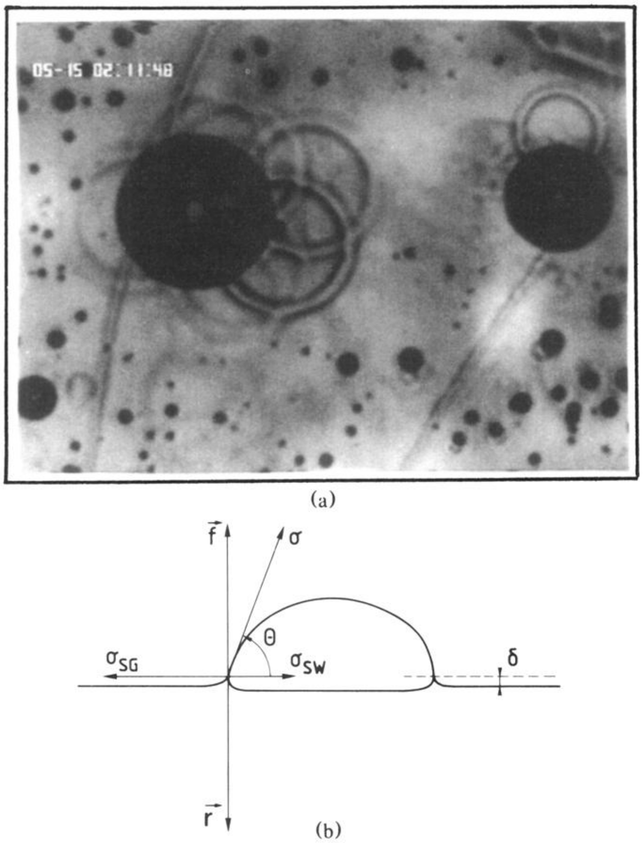

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