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Jumping droplets

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The observations of Steyer, Guenoun, and Beysens [Phys. Rev. Lett. **68**, 64 (1992)] of jumping droplets of water condensed on solid cyclohexane slightly below its melting temperature require, on energetic grounds, the sudden release of surface energy; elastic energy is inadequate. The observed jumps result from rolling a droplet onto, or off of, a thin pool of melted substrate. The phenomenology is predicted to depend on differences of surface energies and on the temperature. The residual rings may be explained by freezing of melt or by plastic flow, and their fading, by flow in a surface melt layer.

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Steyer, Guenoun, and Beysens [1] reported experiments in which water vapor condensed on solid cyclohexane slightly below its melting point. They observed the water droplets making sudden jumps to new positions which overlap their immediate predecessors. The vacated positions of droplets are revealed by residual rings which gradually fade.

The explanation of these experiments requires estimates of the various contributions to the energy of a water drop on a solid cyclohexane substrate. A schematic view of such a drop is shown in Fig. 1(b) of Ref. [1]. The surface energy $E_s \approx 4\pi\gamma r^2 \approx 10^{-2}$ erg, where r is the drop radius (here taken as 30 μm) and γ (taken as 70 erg/cm^2) is a surface tension; I do not yet distinguish among drop-vapor, drop-solid substrate, and drop-melted substrate interfaces.

The elastic energy of deformation of the solid cyclohexane substrate is simply estimated. The normal force per unit length $\gamma \sin\theta$ along the contact line, where θ is the contact angle, produces a stress $\sigma \approx \gamma/(\pi s)$ in the substrate at a distance $s < r$ from the line. The elastic energy attributable to this stress field is

$$E_{\rm el} \approx 2\pi r \int_a^r \frac{\sigma^2}{2C}\pi s \, ds \approx \frac{r\gamma^2}{C}\ln(r/a) \approx 3\times10^{-9}\ \text{erg}\ , \quad (1)$$

where C (taken as 10^{10} erg/cm^3) is a suitably weighted average of the elastic constants of solid cyclohexane (the measured elastic constants [2] are adiabatic, but the more appropriate isothermal elastic constants should be comparable). The lower cutoff a results from plastic flow at the contact line, or is of molecular dimensions in the absence of plastic flow. The upper cutoff r results from the geometry of a circular contact line of radius r and the counterbalancing of the tension exerted at the contact line by the increased pressure inside the droplet; there is, of course, no net force between the droplet and the substrate.

The fact that successive drop positions overlap implies that a drop remains in contact with the substrate, and that its motion is rolling rather than leaping. Because a drop has a finite contact area with a flat substrate, rolling requires an internal shear flow. The viscous dissipation in rolling a drop by roughly its own radius (the magnitude of the observed jumps), maintaining its (aspherical) shape and area of contact with the substrate is $E_v \approx \eta_d\sqrt{\gamma r^3/\rho} \approx 10^{-5}$ erg, where η_d is the viscosity of the fluid drop and ρ its density, and the rate of rolling is roughly given by the quadrupole capillary oscillation frequency [3] $\omega_2 \approx \sqrt{8\gamma/(\rho r^3)} \approx 10^5$ sec^{-1}, consistent with the apparently instantaneous jumps.

The ordering $E_{\rm el} \ll E_v \ll E_s$ implies that elastic energy cannot be driving the jumps of the drops; if they were to move without shear (to avoid the viscous losses) they would break contact between their flattened bottom surfaces and the substrate, incurring an energy cost $E_s \gg E_v$. It is therefore likely that melting powers the jumps by changing the surface energy, rather than by releasing elastic energy. If this is true then the jumping phenomenon should depend on the sign and magnitude of the difference in surface energies $\Delta\gamma \equiv \gamma_{\rm SSC} - \gamma_{\rm LSC} - \gamma_{\rm SSV} + \gamma_{\rm LSV}$, where SS denotes solid substrate, LS liquid substrate, V vapor, and C condensate (water in these experiments). This hypothesis might be tested by experiments with other combinations of materials with different $\Delta\gamma$.

If the contact line crosses a phase boundary on the substrate the equilibrium contact angle changes there. If the contact line were pinned everywhere the actual droplet surface would be nonplanar in the vicinity of the phase boundary, and would depend also on the condensate-vapor surface energy. If it is not pinned, as must be the case on a liquid substrate, then the droplet would move (as well as change its shape) in order to minimize its total energy. A liquid substrate may also move.

The detailed mechanics of the jumps is complex. Slow melting of the substrate would produce a quasistatic relaxation of a drop's shape. The release of surface energy may itself contribute to melting if it is locally dissipated by surface friction, or if following brings warmer fluid (with $T > T_m$, the melting point of cyclohexane) from the upper part of the drop into contact with the substrate.

If $\Delta\gamma > 0$ it is energetically favorable for a droplet to lie

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on the liquid substrate. If melting begins under the droplet (whose upper surface is the source of released heat of condensation) melt will flow to cover the entire contact surface. If melting begins on uncovered substrate the melt may flow under the droplet or the droplet may roll onto the melt pool. The time required for a melt film to flow is $t_f \sim r^2\eta_s/(|\Delta\gamma|l)$, where η_s is the viscosity of the melt and l is the thickness of the film. Guessing $|\Delta\gamma| \approx 70$ erg/cm^2 and $l \sim 10^{-6}$ cm (comparable to the thickness of the surface melt layer [4] present on bare substrate under these conditions) yields $t_f \sim 10^{-3}$ sec.

An elementary estimate shows that the viscous energy dissipated in covering (or removing from) the contact surface a melt layer is $O(E_s)$, and could account for the surface energy released. Although $\omega_2 t_f \sim 10^2$, E_s is so much larger than E_v that even a small deviation from perfectly quasistatic relaxation in the course of film flow may be sufficient to make the droplet roll. Refreezing of the melt where it was attracted to the periphery of the drop's new position may produce the observed [1] residual rings.

If $\Delta\gamma < 0$ it is energetically unfavorable for the droplet to lie on liquid substrate. If melting begins under the droplet melt will flow to uncovered substrate, or the drop may roll off the melt pool. Melt flow may power a jump, just as in the case $\Delta\gamma > 0$. Expulsion of the melt to the periphery of the drop could produce a residual ring.

As T is reduced l decreases rapidly [4] and t_f increases; the film flow mechanism will not lead to jumps at sufficiently low T. A droplet may roll onto or off a melt pool at any T if the condensation rate is high enough to melt substrate. The observation [1] that the residual rings survive being overlain by a droplet implies either that the melt layer is thinner than the ring height or that it only covers a small portion of the contact surface.

Rapid change in a drop's shape, and its subsequent jump, will excite the drop's modes of capillary oscillation. Because the drop remains in contact with the substrate these modes will have dipole character (unlike the familiar modes of a free drop [3]). They will radiate into both the substrate and the gas phases. Observations of this acoustic radiation may be an informative diagnostic of jumps and coalescences, particularly if the wave trains of individual events are observed. The predicted quality factor of the oscillations $Q \sim (8\gamma r\rho/\eta_d^2)^{1/2} \sim 10^2$.

The residual rings might alteratively be the result of forces on the solid substrate. Distributed over molecular dimensions, the normal component of the capillary force at the three-phase boundary line leads to a stress far in excess of the likely yield strength of the substrate. Plastic flow results, permitting all three angles to relax to their equilibrium values, as in the contact of three fluid phases. This explains the fact that the rings appear to be complete uniform circles, which might not be expected if they were the consequence of local melting. At the ring the predicted radius of curvature of the substrate surface $r_c \sim \gamma/\tau$, where τ is its yield strength. It is hard to predict τ, but easy to measure it. The published [1] photograph suggests $r_c \approx 2$ μm, and therefore $\tau \sim 3 \times 10^5$ dyne/cm^2 if the rings are the consequence of plastic flow.

The observed [1] fading of the rings in a time ≈ 1 sec is also interesting. A plausible explanation is flow through the surface melt layer, which will be present in these experiments close to T_m. The strongly curved ridges (producing the visible rings) left behind by a drop are thermodynamically disfavored compared to a flat surface. An elementary argument shows that the matter will flow in the surface melt layer from regions of higher curvature to those of lower curvature, with a characteristic smoothing time of $t_s \approx \eta_s r_c^4/(\gamma l^3)$. Again, arbitrarily taking γ for wetted solid cyclohexane to be comparable to that of liquid water yields $t \approx 1$ sec for $l \approx 60$ Å, as expected [4] a few degrees below T_m. Because of the dependence of l on T, this hypothesis may be tested by measuring the rate at which the rings fade as a function of T. Alternatively, the rings could fade because of evaporation of the substrate, a process which has a characteristically different dependence on T.

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