

Drop Formation by Thermal Fluctuations at an Ultralow Surface Tension

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We present experimental evidence that drop breakup is caused by thermal noise in a system with a surface tension that is more than 10^6 times smaller than that of water. We observe that at very small scales classical hydrodynamics breaks down and the characteristic signatures of pinch-off due to thermal noise are observed. Surprisingly, the noise makes the drop size distribution more uniform, by suppressing the formation of satellite droplets of the smallest sizes. The crossover between deterministic hydrodynamic motion and stochastic thermally driven motion has repercussions for our understanding of small-scale hydrodynamics, important in many problems such as micro- or nanofluidics and interfacial singularities.

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Drop formation represents a basic phenomenon important in a wide variety of industrial and natural processes. For instance, all spraying processes, ranging from dispersing pesticides [1] to ink-jet printing, rely on controlling drop sizes for efficient application. Classically, two hydrodynamic mechanisms of drop formation are known: Surface tension always causes the breakup and is countered by either the viscosity or the inertia of the liquid [2–6].

In this Letter, we report on a different mechanism: drop formation when altered by perturbations of the interface. This leads to both qualitatively and quantitatively different behavior. It has been shown before that finite amplitude perturbations may trigger successive instabilities and qualitatively change the shape of the breakup [7,8]. In our experiments, however, the perturbations are an intrinsic property of the fluid interface: The thermal fluctuations of the interface lead to a new breakup mechanism [9,10]. Such thermal capillary waves are always present at all fluid interfaces due to the thermal energy $k_B T$, with Boltzmann's constant k_B and temperature T .

To estimate at what length scales the thermal noise becomes dominant over capillary forces, a fluctuating stress S is added to the Navier-Stokes equation. Dimensional analysis gives the pressure gradient $\nabla p = \gamma/L^2$, with γ the interfacial tension and L a characteristic length, and the gradient in the fluctuating stress tensor

$$\nabla S \propto \frac{1}{L} \sqrt{\frac{k_B T \eta}{L^3 t}}, \quad (1)$$

where η is the viscosity, and the time t is proportional to $L\eta/\gamma$. It now readily follows that at lengths L of the order of the thermal length $L_T = \sqrt{k_B T/\gamma}$ thermal noise dominates the capillary forces. This is also the typical roughness of an interface and results from the competition between

surface tension that tends to keep the interface flat and thermal energy driving the fluctuations. For simple liquids, L_T is typically nanometric. Consequently, the surface is flat at hydrodynamic scales, and free-surface flows such as the one occurring in droplet snapoff are very well described by the Navier-Stokes equation without fluctuations. This hydrodynamic description breaks down when the flow takes place at scales comparable to L_T , which we are able to observe here by strongly decreasing the surface tension and thus increasing L_T .

This change is achieved by using a colloid-polymer mixture in a common solvent. Because of a depletion interaction, the mixture spontaneously phase separates into a colloid-rich phase (a colloidal “liquid”) and a polymer-rich phase (a colloidal “gas”) at sufficiently high concentrations [11,12]. It then behaves analogously to a two fluid system with, however, an extremely small surface tension. For colloids of diameter d , one typically has $\gamma \sim k_B T/d^2$ [13,14], thus giving $L_T \gtrsim d$, which represents a large surface roughness directly observable by optical microscopy [15]. We use here two different mixtures consisting of poly(methyl methacrylate) colloids with $d = 142$ nm mixed with polystyrene polymers in decalin (system S1) and silica colloids with $d = 26$ nm mixed with poly(dimethylsiloxane) polymers in cyclohexane (system S2). Both systems have been extensively characterized elsewhere [15–17]. We measured the gas-liquid surface tension by analyzing the capillary rise against a glass wall (S1 and S2) [16,17] and the capillary wave spectrum (S1) [15,17]. The measured tension is 20 (S1) and 500 nN/m (S2) for the two mixtures considered here, i.e., 5–6 orders of magnitude smaller than for water ($\gamma = 0.072$ N/m). As a result, the thermal length is very large: For system S1, $L_T \sim 0.45$ μm , and for system S2, $L_T \sim 0.09$ μm .

The formation of drops happens spontaneously after the phase separation of the mixtures into the two coexisting phases [17]. During the demixing, the colloid-rich phase is present at the macroscopic interface with the air in the sample tube. Subsequently, the denser colloid-rich phase drips through the polymer-rich phase, stretching a neck of fluid that breaks at its lower extremity, thus producing a droplet (Fig. 1). The droplets formed in this primary process are of nearly identical size with radii of the order of the capillary length $L_c = \sqrt{\gamma/\Delta\rho g}$, with $\Delta\rho$ the gas-liquid density difference and g the gravitational acceleration. For our systems, L_c lies between 8 and 20 μm . The primary breakup is followed by secondary processes, in which the fluid neck remaining after the first droplet has detached breaks into smaller droplets and at its base.

It is directly evident from the images that for the low surface tension system *S1* the snapoff is significantly different from a regular viscocapillary breakup: The profile is close to symmetric near the rupture point, especially for the secondary events; see Figs. 1(a) and 2. Note that, due to the small scales and low velocities, inertia is completely negligible here. If the breakup were viscous, a slender filament attached to the nearly flat interface of the drop would be expected, forming a very asymmetric double cone, similar to what can be observed in system *S2* [Fig. 1(b)]; hydro-

dynamics predicts that, for our viscosity ratio of order 1, the opening angles of the asymmetric double cone connecting the filament to the drop should then be $\sim 12^\circ$ at the filament and $\sim 156^\circ$ at the drop [18]. In contrast, for the lowest surface tension our experiment yields angles close to 30° on both sides of the breakup point. Recent simulations [9] and theory [10] indicate that the symmetric shape of the pinch region is the signature of a regime in which thermal fluctuations dominate the breakup, in agreement with our findings.

The most striking feature that results directly from the symmetry of the profiles is the absence of very small satellite drops. For viscous breakup, these are ubiquitous and usually form between the filament and the droplet. They are often a source of problems in applications such as spraying processes [19], because they considerably widen the drop size distribution. In our experiments, the noise therefore rather surprisingly narrows the size distribution of the droplets. In contrast, when the surface tension is increased by an order of magnitude (system *S2*), we recover some of the qualitative features of the viscocapillary breakup, i.e., necks breaking into drops connected with long threads that inevitably generate many satellite drops of different sizes. Histograms of the size distribution (Fig. 3) clearly show that for a relatively large surface tension (system *S2*) many very small satellite drops are

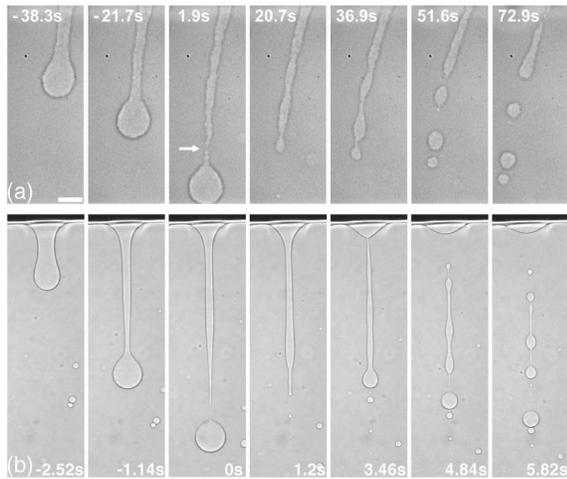


FIG. 1. Image sequences of the breakup events in systems (a) *S1* and (b) *S2*. The breakup of the primary drop is taken as a time reference for the sequences. (a) A large primary drop of nearly 15 μm in diameter moves downwards, stretching behind itself a neck of fluid. When the neck size becomes of order L_T , it breaks at a random point, typically a few micrometers away from the base of the drop (indicated by the arrow). After the primary drop has detached, secondary instabilities develop. The scale bar represents 10 μm . In (b), the snapoff is clearly different than in (a). A long filament attached to a nearly spherical drop is formed. After the first pinch-off, the liquid filament breaks up in the top. The image height is 154 μm . Note the differences in time scales between the two events. See Ref. [24] for accompanying movies of the two events.

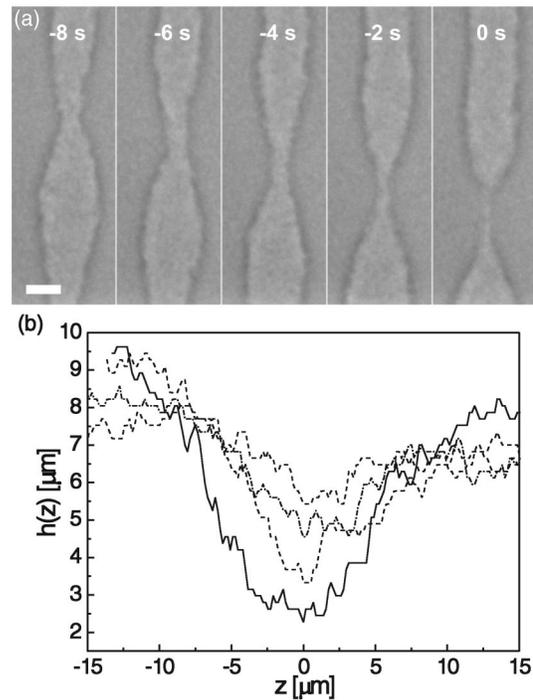


FIG. 2. A typical secondary breakup event for system *S1*. (a) Image sequence showing the symmetry of the profile. The scale bar represents 5 μm . (b) Corresponding neck profiles taken at 3 (solid curve), 15 (dashed curve), 27 (dashed-dotted curve), and 39 s (dotted curve) before breakup. The minimum of each profile has been centered on $z = 0$ for clarity.

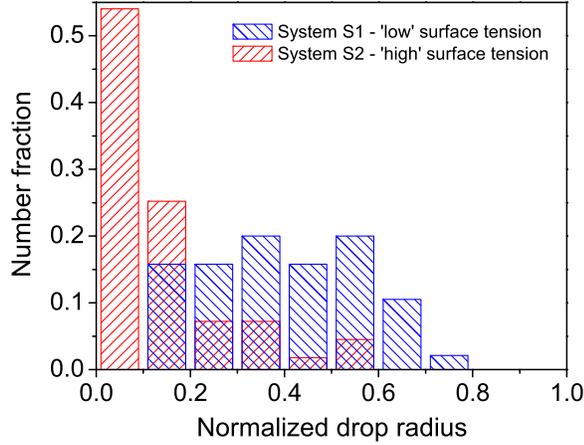


FIG. 3 (color online). Satellite drop size distribution for systems S1 (blue) and S2 (red) after breakup of a primary drop. For the system with the lower surface tension, 18 primary drop events were analyzed, whereas only 5 in the case of the higher surface tension, but the total number of satellite drops was in both cases ~ 113 . The number fraction is with respect to the total number of drops, and the drop radius is normalized by the radius of the primary drop.

formed, whereas for the smaller surface tension (system S1) no small satellite droplets are formed at all. Even more impressive is that the total number of secondary drops decreases considerably, by a factor of ~ 4 , when the noise becomes important.

To quantitatively characterize the breakup singularity, we follow the neck profile and its minimal cross section as a function of time $h_{\min}(t)$, for both “primary” and “secondary” breakups; see Fig. 4. Unexpectedly, our experiment shows that the rate of thinning increases first slowly, especially for secondary events, and then more dramatically just before breakup. This contradicts predictions for viscous deterministic pinch-off, where a linear time dependence $h_{\min} \propto (t_p - t)$, with t_p the time at which pinching occurs, is expected [2,4]. Indeed, estimation of the characteristic length and time scales for typical colloid-polymer mixtures such as our two systems shows that the dynamics is viscous and should be described by Stokes flow [17]. Rather than such a linear time dependence, our observations suggest a power law behavior near the singularity $h_{\min} \propto (t_p - t)^\alpha$, with $\alpha < 1$. Qualitatively, all of these features corroborate the picture for fluctuation-driven breakup resulting from simulations of “nanojets” where an increasing rate of pinching is observed [9] and from the predictions of a power law time dependence for fluctuation-driven pinch-off with $\alpha = 0.42$ [10]. However, attempts to fit primary and secondary events with a power law result in a broad range of exponents. In fact, one readily sees, comparing the two types of events, that $h_{\min}(t)$ differs greatly away from the pinching time but seems to converge towards a unique time dependence as one approaches breakup. We argue here that in some cases and

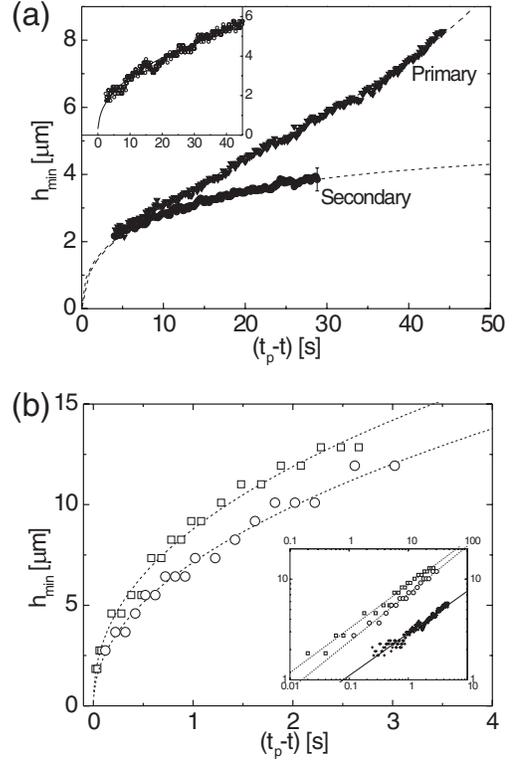


FIG. 4. Time dependence of the minimal neck diameter before breakup. (a) System S1: averages of several events (primary and secondary) overlapping within experimental scatter. The uncertainty in $t_p - t \leq 1$ s. Dashed lines are fits from (4) with $\alpha = 0.42$ fixed. Inset: A single secondary event where gravity and recoil turned out to be unimportant. The solid line follows from the Eggers prediction with $\alpha = 0.42$ [10]. (b) Secondary events. Two events are shown for system S2 (open symbols) for which gravity was not important (detachment of the filament at its base). The uncertainty in $t_p - t \leq 0.04$ s. Best fits yield exponents 0.43 ± 0.01 (triangles) and 0.47 ± 0.02 (circles). Inset: The same data on a log-log plot (x and y axes, bottom and left). For comparison, crosses correspond to the inset in (a) for S1 with an exponent of 0.42 (x and y axes, top and right).

especially for the primary events the breakup is complicated by gravitational stretching or recoil of the filament. The potential importance of gravity has been recognized earlier theoretically by Henderson *et al.* [20]. The fact that gravity is important for our primary events follows from the Bond number Bo , the ratio between gravity and capillarity:

$$Bo = \frac{\Delta\rho R^2 g}{\gamma} = \left(\frac{R}{L_c}\right)^2, \quad (2)$$

with R the radius of the neck. Typically, for our systems one has $R \sim L_c$ and $Bo \sim 1$ when the first drop starts falling, which explains why the neck is at first always thinning faster for primary than for secondary events.

To characterize events that are dominated by the fluctuations, we first focus on events with a small Bond number.

Examples are shown in Figs. 4(a) (insets) and 4(b) and correspond to secondary breakup events in systems $S1$ and $S2$. That gravity is not important for these events also follows from the observation that the filament remains nearly at the same height during these events; see Fig. 1. The dependence of the radius on the time distance from snapoff can be described by a power law $\alpha \sim 0.42$, in excellent agreement with the predictions of Eggers for fluctuation-induced breakup. Interestingly, we observe this power law dependence also for the system with the relatively large surface tension, system $S2$, where we can follow the breakup over more decades in time and find that $\alpha = 0.45 \pm 0.04$, although the qualitative features are more reminiscent of regular viscocapillary breakup. Possibly, some of the effects of thermal noise already show up in $h_{\min}(t)$.

To quantify the effect of gravity, we consider a fluid cylinder of diameter h , length l , and volume V stretched by gravity at a constant rate along its axis such that $l(t) = vt + l_0$, with v a constant “sedimentation” velocity and l_0 a start filament length; volume conservation gives $h(t) = 2\sqrt{V/\pi l(t)}$. Close to pinch-off, we assume $h \propto (t_p - t)^\alpha$. We now propose a crossover formula between a regime in which the fluid cylinder is stretched mainly by gravity, and thins accordingly, and a regime dominated by thermal fluctuations. One has

$$h_{\min}(t) \propto \left(\frac{V}{\pi(vt + l_0)} \right)^{1/2} (t_p - t)^\alpha, \quad (3)$$

and, rearranging with $x = t_p - t$ and $\bar{x} = t_p + l_0/v$, one obtains

$$h_{\min}(x) \propto x^\alpha / (\bar{x} - x)^{1/2}. \quad (4)$$

Recoil of the filament, on the contrary, may oppose a force effectively slowing down the breakup process in secondary events. This can be accounted for by changing the sign in the denominator of (4) [20]. Equation (4) yields a perfect fit to the data [Fig. 4(a)] demonstrating the crossover from gravity to thermal noise.

In summary, we studied a novel thermal noise-induced mechanism of drop formation; at ultralow surface tension, this is completely different than the regular viscocapillary breakup. Increasing the surface tension by an order of magnitude shows qualitatively some of the viscocapillary and quantitatively some of the noise features. The precise point of crossover between deterministic hydrodynamic and stochastic thermally driven motion is difficult to obtain experimentally and may be worthwhile to explore theoretically. The thermal noise-induced mechanism also applies for molecular fluids, although at nanometric length scales. Indeed, our pictures are strikingly similar to those of simulated breakup of nanometric jets (nanojets) [9], emphasizing the universality of our findings. This has repercussions for our understanding of all hydrodynamic processes happening at small scales, e.g., nanofluidics,

droplet coalescence, air entrainment in liquids, etc., and modifications of the classical equations are required as shown in recent theoretical work on thin film flows [21–23]. As noted in Ref. [22] and shown here, colloid-polymer mixtures are attractive candidates for studying such processes.

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- [24] See EPAPS Document No. E-PRLTAO-97-013650 for movies of the breakup of drops in demixed colloid-polymer systems. For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.