Persistence of memory in drop breakup: The breakdown of universality

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A low-viscosity drop breaking apart inside a viscous fluid is encountered whenever air bubbles, entrained in thick syrup or honey, rise and break apart. Experiment, simulation and theory show that the breakup in the situation where the interior viscosity can be neglected produces an exceptional form of singularity. In contrast to previous studies of drop breakup, universality is violated so that the final shape at breakup retains an imprint of the initial and boundary conditions. A finite interior viscosity, no matter how small, cuts off this form of singularity and produces an unexpectedly long and slender thread. If exterior viscosity is large enough, however, the cut-off does not occur because the minimum drop radius reaches sub-atomic dimensions first.

Underlying one of the common occurrences of daily life, the breakup of a liquid drop, is a rich and beautiful phenomenon. As a drop divides the neck connecting the different masses of fluid necessarily becomes arbitrarily thin with a curvature that grows without bound until molecular scales are reached. Since surface tension gives rise to a pressure proportional to the curvature, this pressure also diverge. Similar singularities, where a physical quantity effectively diverges, occur in many different realms ranging from the sub-atomic—nuclear fission (*1*), to the celestial—star formation (*2*). The ubiquity, simplicity and accessibility of drop breakup makes it an ideal test-bed for studying divergent dynamical behavior occurring elsewhere in nature.

Near such a singularity, the dynamics are normally governed by the proximity to the singularity itself and the dynamics becomes universal so that all memory of initial and boundary conditions is lost. In such cases, the breakup becomes scale-invariant; upon appropriate rescaling, drop shapes near snapoff can be superimposed at different times onto a single form, depending on only a few material parameters (*3*–*5*).

Here we report an important exception to this class of behavior: the breakup of a zero-viscosity drop inside an extremely viscous exterior fluid produces an unexpected, non-universal form of singularity, in which the memory of the initial conditions persists throughout the breakup process. Axial structure imposed at the outset on large length scales remains as the thin neck collapses. The unusual character of this breakup suggests a novel and controllable method for producing sub-micron structures.

Because all classical fluids have a finite viscosity, it is important to understand what will be the nature of the singularity when the interior viscosity is very small but non-zero. If the interior viscosity is sufficiently small, as for an air bubble in syrup, the zero-viscosity drop breakup dynamics persist down to the atomic scales. However, if the interior viscosity is large enough, or the exterior viscosity small enough, the singularity will be cut-off. In this case, the large-scale shape of the drop takes on an unexpected appearance. The smooth profile is transformed into a long and thin thread, whose thickness can be less than $1\ \mu$m. The drop and surrounding fluid in our experiment are chosen to display the zero-viscosity drop breakup dynamics, which remembers initial and boundary conditions, and the subsequent destruction of this dynamics by the effect of a finite drop viscosity.

Fig. 1 shows a water drop with a viscosity $\mu_{\rm int} = 0.01$ poise (1 poise = 1 g/(cm ·s)) as it drips through silicone oil (poly-dimethylsiloxane) with a viscosity of $\mu_{\rm ext} = 120$ poise. In Fig. 1A to 1C, the drop shape near the minimum forms a quadratic profile that remains smooth and symmetric about the minimum as the neck collapses radially. This quadratic regime, with constant axial curvature, persists until the neck thins to a radius of about a hundred microns at which point the thinning of the neck slows dramatically. The slowing begins at the minimun and propagates axially so that a thin thread is formed connecting two conical regions of the drop as shown in Fig. 1D and 1E. Finally the drop breaks at the two ends of the thread.

In both experiments and simulations we investigate the dynamics of the quadratic breakup regime (Fig. 1A to 1C) by measuring the radius of the drop profile, $h(z,t)$, as a function of z, the axial position measured from the minimum value of h, and time t. We use the finite-element method to simulate the breakup by solving the Navier-Stokes equations for the interior and exterior flows. Instead of a dripping drop, the simulation tracks how a sinusoidal perturbation on a liquid cylinder causes the cylinder to breakup. The algorithm has successfully captured the breakup dynamics for drops of varying viscosities dripping through air, including the successive creation of satellite droplets (*6, 7*). Fig. 2 shows κ, the axial curvature at the minimum, plotted versus $h_{\rm min}$ for two experiments with slightly different nozzle diameters and two simulations with significantly different initial perturbations. In all four cases, the axial curvature approaches constant values at small $h_{\rm min}$. Thus, near its minium, the neck shape is collasping with a uniform radial velocity. Unexpectedly, different initial conditions and boundary conditions lead to different asymptotic axial curvatures. This suggests that the quadratic regime corresponds to a breakup which does not result in a universal profile, but instead remembers the quadratic profile near the minimum imposed by the initial and boundary conditions.

To investigate this unusual behavior, we examine the simulation and find the leading order force balance to be between surface tension and exterior viscous stress. This force balance gives rise to a collapse velocity proportional to $\gamma/\mu_{\rm ext}$, which is independent of abosolute length-scale. This is why the minimum radius, $h_{\rm min}$, decreases linearly with time in both experiments and simulations. We next examine the pressure profile from the simulation and find that the interior pressure is virtually uniform in space, varying by less than 0.02% over the entire drop (Fig. 3 insert). The absence of a pressure gradient indicates that the interior flow, and therefore also the interior inertia, are negligible. The drop interior thus behaves as if it were static.

Previous studies have shown the drop breaks only as fast as the surface tension effects can squeeze interior fluid out of the thinning neck (*3, 4, 8*). As a consequence, the breakup obeys a local volume-flux conservation law. In the regime just discussed, this conservation law is irrevelant to the dynamics. The drop breaks only as fast as the surface tension effect can induce the exterior flow to collapse inward. Interior flow effects are negligible. The local volume-flux conservation law previously relevant for breakup is transformed into a condition of uniform interior pressure.

The idea described above is captured quantitatively by a simple model of $\mu_{\rm int} = 0$ breakup. We take advantage of the fact that the quadratic profile near the minimum is long and slender, so that the breakup dynamics are well-approximated by the collapse of a hollow cylinder inside a viscous fluid. We model the exterior velocity field as due to a line of point sinks situated along the drop centerline. The strength of the sinks is determined by requiring that, at the surface, the velocity of the exterior fluid equals the collapse velocity of the drop. This allows us to derive an expression for the exterior viscous stress on the drop surface. Balancing the exterior viscous stress against surface-tension pressure and interior pressure yields the evolution equation for the drop profile

$$\frac{2\mu_{\mathrm{ext}}}{h(z,t)}\frac{\partial h(z,t)}{\partial t} - P(t) + \frac{\gamma}{h(z,t)} = 0 \qquad (1)$$

The first term corresponds to the exterior viscous stress, the second term corresponds to the interior pressure, and the third term corresponds to the surface tension pressure. The reference pressure is the exterior pressure far from the breaking drop. The steady-state version of (1) was first derived by Buckmaster (*9*). The interior pressure $P(t)$ is related to the drop profile via an integral which constrains the drop volume to be constant over time (*10*). Thus the drop shape evolution is in general nonlinear, even with this simple model. However, a drastic simplification occurs near breakup because $P(t)$ is bounded and becomes progressively unimportant compared with the exterior viscous stress and the surface tension pressure, both of which diverge. Moreover, the divergences in the two stresses cancel in an unusually simple way, resulting in the entire profile collapsing with a radial velocity, $\gamma/2\mu_{\mathrm{ext}}$, which is independent of axial position. The generic initial condition, which is a quadratic shape near the minimum, is preserved until breakup.

This model enables us to draw several important conclusions about the breakup dynamics. Since all points on the surface move radially inward with the same velocity, the axial length-scale does not vary as h_{min} goes to 0. The breakup is not self-similar. This is also why, as shown in Fig. 2, the axial curvature at the minimum, κ, which is inversely proportional to the typical axial length-scale, z_0, remains constant as h_{min} decreases to 0 (*11*). Since the breakup region does not change in the axial direction, the profile forgets neither the initial nor the boundary conditions imposed. Thus the final breakup profile is non-universal (Fig. 2).

In contrast, previously studied examples of drop breakup produce nonlinear dynamics, so that the drop shape is invariant within a contracting region characterized by a decreasing radial length-scale, h_{min}, and a decreasing axial length-scale, z_0. Since this region contracts to a point at breakup, the drop shape outside the region is linked together discontinously, creating a kink instead of the smooth quadratic profile observed here. Most importantly, the scale-invariant dynamics erases all memory of initial and boundary conditions while the spatially uniform radial collapse considered here allows a memory of the initial and boundary conditions to persist through breakup.

We now consider how a nonzero interior viscosity can cut off this quadratic regime. The retarding effect of viscous dissipation associated with the interior fluid having to squeeze out of a thinning neck, initially negligible, becomes significant close to breakup. We can estimate the interior viscous dissipation during the quadratic breakup regime. The size of the interior velocity, U_{int}, is set by the local volume-flux conservation, $\pi h_{\min}^2 U_{\mathrm{int}} \approx z_0 2\pi h_{\min}(\mathrm{d}h_{\min}/\mathrm{d}t)$, which requires the local thinning of the thread, $\mathrm{d}h_{\min}/\mathrm{d}t$, be balanced by the axial flow out of the local region. The resultant estimate for U_{int} shows the interior viscous stress, $\mu_{\mathrm{int}} U_{\mathrm{int}}/h_{\min}$, increases as $h_{\min}^{-2}$, which is more rapid than the $h_{\min}^{-1}$ divergence of the surface tension pressure. We can check this argument by looking at the simulation for the perturbed cylinder. This shows the maximum interior pressure, which has one contribution from global volume conservation and another from interior viscous dissipation, indeed increases as $h_{\min}^{-2}$ and becomes comparable with surface tension pressure as $h_{\min}$ decreases to h_{cutoff}, the cut-off radius (Fig. 3). Above h_{cutoff}, our simulations show interior viscous dissipation is indeed negligibly small, consistent with the model presented above. Below h_{cutoff}, breakup is expected to slow significantly, as the viscous resistance has a large contribution from the interior flow in addition to the exterior flow. The scaling argument also predicts h_{cutoff} is roughly a factor $\mu_{\mathrm{int}}/\mu_{\mathrm{ext}}$ smaller than the initial drop radius. For a drop 1 cm in radius and $\mu_{\mathrm{int}}/\mu_{\mathrm{ext}}$ values which are 10^{-8} or less, the quadratic breakup regime persists down to a minimum radius of a few angstroms, by which point the continuum approximation breaks down. At such small values of $\mu_{\mathrm{int}}/\mu_{\mathrm{ext}}$, as is the case for an air bubble in syrup, breakup is then entirely in the asymptotic $\mu_{\mathrm{int}} = 0$ regime, one for which our quadratic breakup analysis would hold throughout the entire process.

For larger values of $\mu_{\rm int}/\mu_{\rm ext}$, the finite viscosity of the drop brings out a qualitative change in the large-scale structure of the drop profile (Fig. 1D & 1E). Unfortunately this change, which occurs around $h_{\rm cutoff}$, lies outside the simulation range for $\mu_{\rm int}/\mu_{\rm ext} = 10^{-4}$. To view this regime, we perform the simulation at $\mu_{\rm int}/\mu_{\rm ext} = 10^{-3}$ which has a larger $h_{\rm cutoff}$. Fig. 4A shows the behavior for the larger $\mu_{\rm int}/\mu_{\rm ext}$ and clearly demonstrates that the interior pressure does not increase above the surface tension pressure. As the breakup enters the new regime, the two minima move apart as $\sqrt{h_{\rm cutoff} - h_{\rm min}}$ (Fig. 4B). Fig. 4C shows the development of a double peak in the interior pressure profile. The results in Fig. 4B and 4C are consistent with the idea that the initially quadratic profile is slowed down and blunted by the interior viscous stresses which can no longer be neglected below $h_{\rm cutoff}$. We note that the values of $h_{\rm cutoff}$ in our cylinder breakup simulation are smaller than those observed in the falling drop experiment, probably because of the difference in boundary and initial condition and because of additional stresses created by the falling drop. However we emphasize that the dimensionless aspect ratio, in contrast to $h_{\rm cutoff}$, for the thin thread in the experiment is within experimental error of that obtained from the scaling argument. Finally, the drop breaks under a balance of interior and exterior viscous stresses and surface tension, a regime previously shown to give rise to universal breakup profiles in the form of two connected cones (*4, 12–15*).

Direct comparison of the cross-over behavior between the simulation and the experiment is diffcult, because the different initial and boundary conditions employed influence the final outcome. The 8 μm radius of the thin thread observed in the dripping experiment (Fig. 1E) is slightly larger than that observed in the cylinder breakup simulation. The thread aspect-ratio (radius/length), a quantity in which effects associated with absolute size largely canel, is roughly 200, which is about the same order as the value of 100 from the scaling argument. Finally, the drop breaks under a balance of interior and exterior viscous stresses and surface tension, a regime previously shown to give rise to universal breakup profiles in the form of two connected cones (*4, 12–15*).

Both aspects of the breakup process, the reproduction of the initial profile on smaller ones during the quadratic regime, and the subsequent formation of a long, thin thread are controllable. The large exterior viscosity also damps out noise from the environment, unlike other examples (*8*). Moreover, the evolution of structure is slow. If the outer viscosity is $2 \cdot 10^5$ poise, then we estimate that the minimum diameter of a 0.2 poise drop decreases at the rate of 3 μm/sec, and creates a thin thread with radius of 0.1 μm. A 1 cm drop of 0.2 poise fluid in a $2 \cdot 10^5$ poise surrounding fluid breaks at the rate of 3 μm/s and creates a thread whose radius is roughly 100 nm. A thin solid thread could thus be manufactured by adding a pre-polymer (which does not change the viscosity or the rheology) to the inner fluid, and then rapidly photopolymerizing it during the appropriate stage of breakup. If we assume that bulk polymerization rates (*16*) are relevant for the geometry of a thin thread, then the slow rate of collapse should allow ample time for the thread to solidify. This is being attempted for encapsulation (*17*). For coating technologies where air entrainment in viscous fluids is an issue (*18–20*), our study suggests the entrained bubble size distribution can be tuned by increasing the exterior viscosity. Increasing the exterior viscosity so that the breakup dynamics lies entirely in the quadratic regime also eliminates satellite drops, thereby making it possible to manufacture monodisperse gas bubbles in a viscous flow, in analogy with techniques being developed to manufacture such bubbles in inertial flows (*21*). The viscous flow regime is relevant for the processing of foods, pharmaceuticals and metal foams.

In conclusion, we observe non-universal, linear dynamics accompanying the formation of a smooth singularity in the breakup of a water drop in viscous silicone oil. This is the asymptotic regime for small enough values of $\mu_{\rm int}/\mu_{\rm ext}$ so that the interior viscosity can be neglected throughout the breakup process. For larger $\mu_{\rm int}/\mu_{\rm ext}$, the interior viscosity becomes important before atomic-dimensions are reached. This produces a long and thin thread. The linear dynamics associated with the formation of a singularity demonstrates that there are two ways for the formation of a singularity to simplify dynamics. In the generic case, the singularity dynamics become scale-invariant, confined to a region which shrinks in all dimensions, thereby erasing all memory of boundary and initial conditions. In the case studied here, dynamics near the singularity is characterized by an axially uniform radial collapse, so that the axial length-scale remains constant, thereby making it possible for memory of the initial and boundary conditions to persist.

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10. More precisely, it can be shown that the interior pressure $P(t)$ is given by $P(t) = \pi(\gamma/a^3)\int_{\mathrm{droplength}} h(z,t)\mathrm{d}z$ where a is a typical radial length-scale, chosen to make the dimensionless drop volume equal to 1.

11. For nonlinear breakup dynamics, the axial curvature at the mininum, κ, is related to the typical axial length-scale, z_0 via $\kappa \propto h_{\min}/z_0^2$. Here, $\kappa \propto 1/z_0$ because the linear breakup dynamics do not change the axial curvature.

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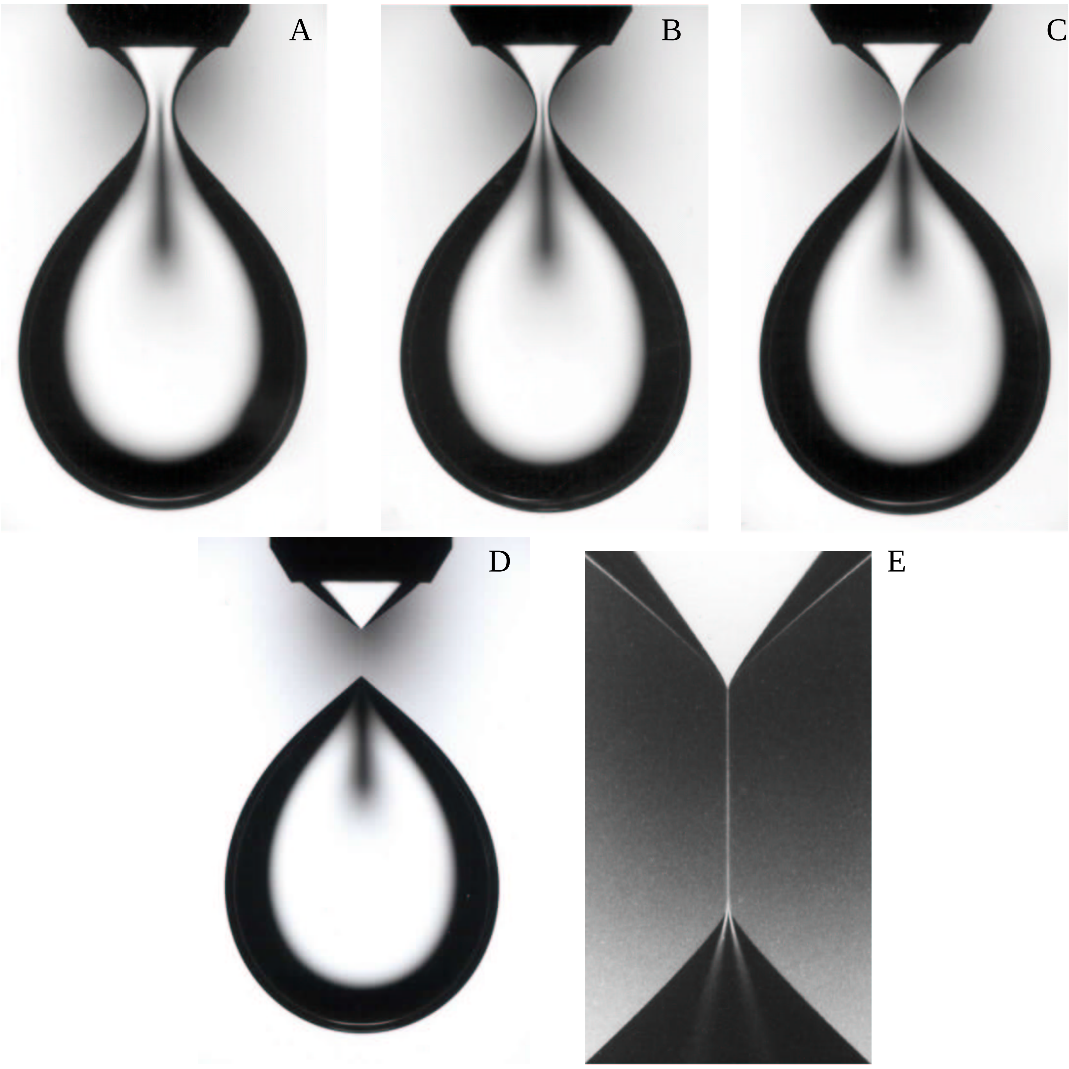

Figure 1: A 10^{-2} poise water drop dripping through 120 poise silicone oil. The inner diameter of the nozzle is 4.7 mm. (A) to (C) Quadratic breakup regime. The quadratic profile near the minimum collapses radially. (D) Effect of drop viscosity alters the drop shape from a quadratic with one minimum to a long and thin thread. (E) A close-up of the 8 μm-radius and 2 mm long thread bridging two conical regions of the drop.

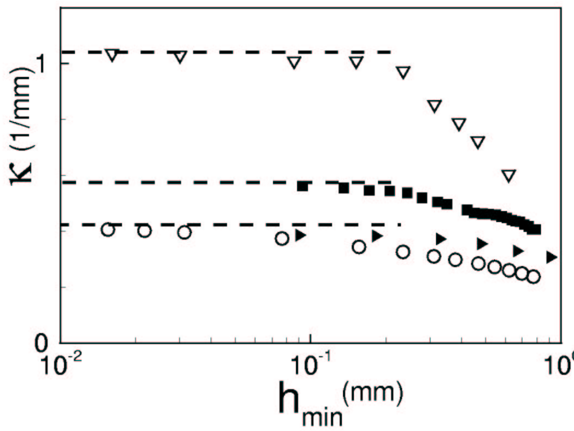

Figure 2: Axial curvature at the minimum, κ, versus $h_{\min}$ for two dripping drop experiments (solid symbols) with slightly different inner nozzle diameters (4.7 mm for solid triangles and 6.2 mm for solid squares) and two cylinder breakup simulations (open symbols) with significantly different initial perturbation wavelengths (3.9 cm for open triangles and 2.2 cm for open circles with average cylinder radius fixed at 6.2 mm). The experimental measurement errors are on the order of the symbol size while the simulation errors are smaller than the symbol size. Different initial or boundary conditions produced different asymptotic axial curvatures.

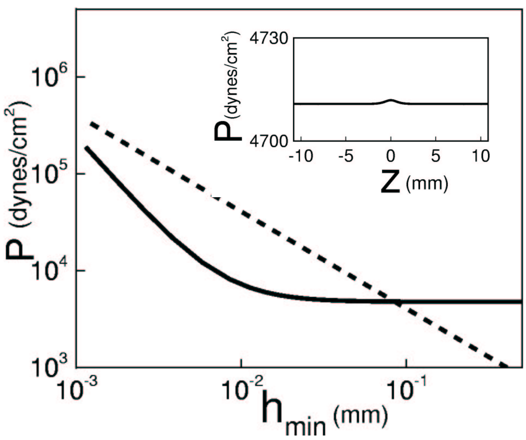

Figure 3: Maximum interior pressure (solid line) and surface tension pressure (dashed line) from simulation of water-in-viscous silicone oil breakup, with $\mu_{\rm int}/\mu_{\rm ext} = 10^{-4}$. The pressure first remains constant, then diverges as $h_{\rm min}^{-2}$. The cut-off radius, $h_{\rm cutoff}$, is approximately 10^{-3} mm from the scaling argument. A scaling argument suggests the cut-off radius, $h_{\rm cutoff}$, is approximately 1 μm, just below the simulation range. The insert shows the interior pressure profile along the drop centerline when $h_{\rm min} = 0.1$ mm. The pressure varies by less than 0.02% over the entire drop. In order to show this slight variation, the range of the pressure displayed has been restricted to a narrow range from 4700 dynes/cm^2 to 4730 dynes/cm^2.

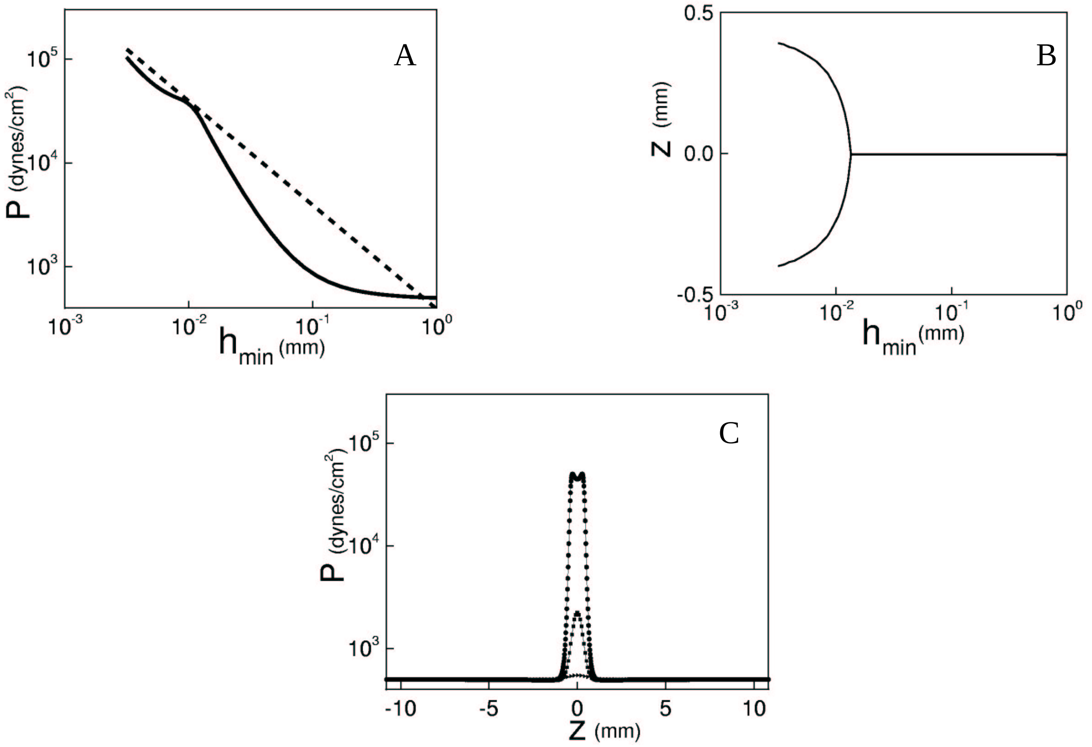

Figure 4: Simulation of breakup for $\mu_{\text{int}}/\mu_{\text{ext}} = 10^{-3}$. (A) Maximum interior pressure (solid line) and surface tension pressure (dashed line). The trend is similar to Fig. 3 except the interior pressure becomes comparable with surface tension pressure at $h_{\text{cutoff}} \approx 10^{-2}$ mm. (B) Axial location of the minimum versus minimum radius. The single minimum splits into two minima, which move apart as $\sqrt{h_{\text{cutoff}} - h_{\text{min}}}$. (C) Interior centerline pressure profiles at $h_{\text{min}} = 0.1$ mm, 0.01 mm and 0.002 mm. The initial spatially uniform pressure develops a pronounced peak as interior viscous dissipation becomes significant. After the minimum splits into two, the pressure develops a double peak.