

Dynamics of Liquid Nanojets

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We study the breakup of a liquid jet a few nanometers in diameter, based on a stochastic differential equation derived recently by Moseler and Landman [Science **289**, 1165 (2000)]. In agreement with their simulations, we confirm that noise qualitatively changes the characteristics of breakup, leading to symmetric profiles. Using the path integral description, we find a self-similar profile that describes the most probable breakup mode. As illustrated by a simple physical argument, noise is the driving force behind pinching, speeding up the breakup to make surface tension irrelevant.

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Given the current trend for miniaturization, it is natural to ask about the behavior of liquids on increasingly small scales, where thermal fluctuations eventually become important. In the case of free surfaces, relevant for all printing and microstructuring applications [1], fluctuations can be expected to be even larger than in confined geometries. Their importance is estimated by comparing the surface tension γ with the thermal energy $k_B T$ per unit area. Thus for structures whose size is in the order of the thermal length scale $\ell_T = (k_B T / \gamma)^{1/2}$ [2], usually about a nm at room temperature, fluctuations should make a leading-order contribution. Predicting the (typical) behavior of fluids on the nanoscale is therefore an extremely challenging statistical physics problem, since the noise can no longer be treated in a standard perturbative fashion [3]. Instead, nonperturbative methods are called for to properly account for thermal fluctuations.

In the absence of experiments that could directly measure fluid flow on the nanoscale, molecular dynamics (MD) [4,5] computations are an ideal tool. Previous analyses of drops and threads [6–8] convincingly showed hydrodynamic behavior on the nanometer scale, and agreement with breakup times and growth rates as predicted by linear theory [9]. Recently [10] a realistic molecular dynamics simulation of a jet of propane issuing from a nozzle 6 nm in diam was performed, which also paid close attention to the nonlinear dynamics close to breakup. Remarkably, a coherent jet develops, from which drops separate at slightly irregular intervals to form a quasistationary decaying state. If nozzles of this size were to be built, this opens fascinating perspectives of transporting current printing and structuring techniques into the nanoworld.

However, a careful analysis of the breakup process revealed [10] that the presence of noise qualitatively alters the character of the breakup. While the deterministic motion at a corresponding Reynolds number forms elongated necks between successive drops [9], noise leads to profiles symmetric around the pinch point. Quite surprisingly, this produces a narrower distribution of drop sizes, as we will discuss in more detail below. In addition, on the nanoscale

the motion of the minimum neck radius accelerates as breakup is approached, while the corresponding time dependence $h_{\min} = 0.03(\gamma\rho/\nu)(t_0 - t)$ is linear for deterministic pinching [11]. Here ν is the kinematic viscosity and ρ the density of the fluid. Thus the theoretical challenge is to understand this qualitative change of behavior in a regime where noise makes the leading contribution.

To deal with the above set of problems, we use the continuum description given by [10], which consists in adding a stochastic term to the lubrication description of a deterministic jet [12]. The amplitude of the noise is fixed by the condition of detailed balance [13]. Detailed numerical simulations of the stochastic equation gave very convincing agreement with MD simulations. This means that hydrodynamics, at least when suitably generalized to include fluctuations, is fully capable of describing free-surface flows down to a scale of nanometers.

The coupled set of differential equations for the radius of the fluid jet $h(z, t)$ and the axial velocity $v(z, t)$, as derived in [10], reads

$$\partial_t h^2 + (h^2 v)' = 0, \quad (1)$$

$$\partial_t (h^2 v) + (h^2 v^2)' = -G' + 3(h^2 v')' + D(hN)', \quad (2)$$

where the prime refers to differentiation with respect to the spatial variable. The first equation (1) expresses mass conservation, (2) is the momentum balance. All quantities are written in units of the intrinsic length and time scales $\ell_\nu = \nu^2 \rho / \gamma$, $t_\nu = \nu^3 \rho^2 / \gamma^2$, respectively. In the numerical simulation reported below, we use periodic boundary conditions for (1) and (2). For a “liquid bridge” [10], i.e., a fluid drop held between two circular plates of radius R , the boundary conditions would be $h = R$ and $v = 0$ at the position of the plates. For later convenience the Laplace pressure term is written in the form $G' = h^2 \kappa'$, κ being the mean curvature of the interface. The Gaussian Langevin force is uncorrelated in space and time,

$$\langle N(z_1, t_1) N(z_2, t_2) \rangle = \delta(z_1 - z_2) \delta(t_1 - t_2), \quad (3)$$

and the dimensionless constant $D = \sqrt{(6/\pi)}\ell_T/\ell_\nu$ measures the strength of the noise contribution.

Since the derivative of the noise is an extremely singular quantity, it is useful to integrate (2) once, setting $P = \int_0^z p(x)dx$, where $p = h^2v$ is the momentum. Thus we arrive at the conserved form of the equations

$$\partial_t h^2 = -P'', \quad (4)$$

$$\partial_t P = -(P'^2/h^2) - G + 3h^2(P'/h^2)' + DhN. \quad (5)$$

Figure 1 shows the collapse of a liquid thread of propane 6 nm in diam as given by (4) and (5) with periodic boundary conditions. The results agree well with the computation shown in the supplementary Fig. 1 of [10], and in particular, the profile remains close to being symmetric. Remembering that P is the velocity of the fluid times a typical volume, the multiplicative factor in front of the random force in (5) corresponds to a relative *increase* in noise strength as pinchoff is approached. This provides us with a simple physical picture for an effective force generated by fluctuations. Namely, a random fluctuation which increases the thread radius also increases its effective mass, slowing down the motion. Any fluctuation towards a smaller neck radius, on the other hand, accelerates the motion. On average, the fluctuations thus drive the thread towards breakup, in fact more effectively than surface tension as we will see below. One should also note the similarity of (5) with the equation describing directed percolation [14].

It is clear that conventional perturbative expansions around the deterministic solution are doomed to fail in describing this mechanism, since the noise makes a dominant contribution. In fact, any average taken at a fixed time no longer makes sense for this problem, because there is a finite probability for pinchoff to have occurred, so the

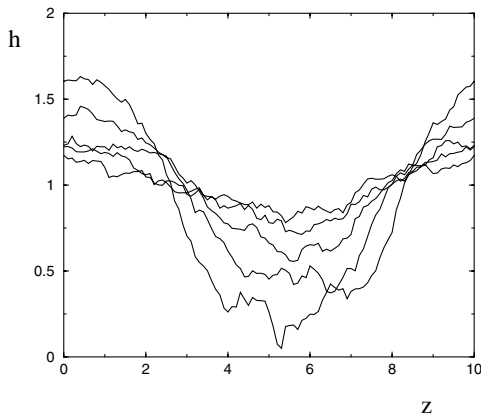


FIG. 1. The computed interface profile of a collapsing bridge of liquid propane at 185 K. All lengths are nondimensionalized by the initial bridge radius of 3 nm. The time interval between the profiles is 150 ps.

original formulation ceases to be valid. Thus a valid description has to be conditioned on the event of breakup to take place at a fixed time t_0 . It is then natural to ask for the *most probable* sequence of profiles that brings one from the initial condition to some final profile at time t_0 , corresponding to a “typical” breakup event. From a standard path integral description, using the Gaussian properties of N , one finds [3] that the probability for such a path is

$$W\{h(z, t), P(z, t)\} \sim \exp\left[-\int_0^{t_0} dt L\right], \quad (6)$$

where the “Lagrangian” is

$$L = \frac{1}{2D^2} \int dz \frac{[\dot{P} + (P'^2/h^2) + G - 3h^2(P'/h^2)']^2}{h^2}. \quad (7)$$

The first equation (4) has no noise in it and has to be treated as a constraint. To find the most probable path *with fixed end points* one derives the Euler-Lagrange equation [15] for the variation in $a = h^2$ and P , with the constraint treated by adding a Lagrange multiplier $\tilde{a}(\dot{a} + P'')$ to L . It is somewhat more convenient to pass to a “Hamiltonian” description, introducing $\tilde{P}(z) = \partial L / \partial \dot{P}(z)$ as the conjugate field, in the literature on critical phenomena also known as the “response” field [16,17]. From this one directly finds the Hamiltonian equations

$$\begin{aligned} \partial_t a &= -P'', & \partial_t P &= -P'^2/a + 3a(P'/a)' + D^2 a \tilde{P}, \\ \partial_t \tilde{a} &= -\frac{D^2}{2} \tilde{P}^2 - \tilde{P} P'^2/a^2 - 3(\tilde{P} P')'/a, \\ \partial_t \tilde{P} &= -2(\tilde{P} P'/a)' - 3[(\tilde{P} a)'/a]' + \tilde{a}''. \end{aligned} \quad (8)$$

The contribution G from surface tension was dropped, since it will turn out below that it is subdominant near the pinch point. Introducing the transformation $\tilde{P} = D^2 \tilde{P}$ and $\tilde{a} = D^2 \tilde{a}$ the amplitude D can be scaled out of the problem.

“Optimal” paths such as those described by (8) have recently enjoyed some popularity in the statistical mechanics literature [18,19]. However, there are two conceptual difficulties associated with (8). The first is that the equation for \tilde{P} contains a term that corresponds to *negative* diffusion, so it cannot be integrated forward in time. In [19] an ingenious yet extremely elaborate computational scheme was developed to deal with this problem, based on an initial guess of the *complete evolution* of the profiles. In subsequent iterations, the physical fields were always integrated forward in time, the conjugate fields backward in time. Another method, based on direct optimization of the functional (7) has very recently been developed [20] for the study of metastable systems. A second, perhaps more serious problem is that one does not know *a priori* what the final profile is supposed to be, so it has to be guessed.

Once a solution is found, the probability of finding a given final profile can be estimated by evaluating the probability of the total path. This evidently amounts to a daunting mathematical problem for a complicated system like (8).

Both problems can simultaneously be dealt with by assuming that the solution is *self-similar*, as found for the deterministic solution [11,21]. This means we assume solutions for small $|t'| = |t_0 - t|$ to be of the form

$$\begin{aligned} a(z, t) &= |t'|^{2\alpha} \phi^2(\xi), & P(z, t) &= |t'|^{2\alpha} \psi(\xi), \\ \bar{a}(z, t) &= |t'|^{-1} \Gamma(\xi), & \bar{P}(z, t) &= |t'|^{-1} \chi(\xi), \\ \xi &= (z - z_0)/|t'|^{1/2}, \end{aligned} \quad (9)$$

where the exponent α remains to be determined. We are thus looking for a solution that breaks at a point z_0 in space. Plugging (9) into (8), one finds the similarity equations

$$\begin{aligned} -2\alpha\phi^2 + \frac{\xi}{2}(\phi^2)' &= -\psi'', \\ -2\alpha\psi + \frac{\xi}{2}\psi' &= -\psi'^2/\phi^2 + 3\phi^2(\psi'/\phi^2)' + \phi^2\chi, \\ \Gamma + \frac{\xi}{2}\Gamma' &= -\frac{1}{2}\chi^2 - \chi\psi'^2/\phi^4 - 3(\chi\psi')'/\phi^2, \\ \chi + \frac{\xi}{2}\chi' &= -2(\chi\psi'/\phi^2)' - 3[(\chi\phi^2)'/\phi^2]' + \Gamma'', \end{aligned} \quad (10)$$

where now the prime refers to differentiation with respect to ξ . One notices immediately that (10) is invariant under the transformation $\phi \rightarrow A\phi$ and $\psi \rightarrow A^2\psi$, so in the following it is enough to look for solutions with $\phi(0) = 1$.

Physically meaningful solutions of the set (10) must match onto an outer solution that is slowly varying on the local time scale set by $|t'|$ [11], which means that $|t'|$ must drop out of the similarity description for large arguments $\xi \rightarrow \pm\infty$. For the profile ϕ this means that it must grow like $\phi \sim \xi^{2\alpha}$ at infinity. We are looking for *symmetric* solutions of (10), which were found not to exist for its deterministic counterpart [11]. Amazingly, we found that the subset of solutions of (10) with the correct asymptotic behavior obey the second order *linear* equation

$$\psi'' = \frac{2\alpha}{3}\psi - \frac{\xi}{6}\psi', \quad (11)$$

and the other functions can be written in terms of ψ as follows:

$$\phi^2 = \psi/3, \quad \Gamma = -27(\psi'/\psi)^2, \quad \chi = -18(\psi'/\psi)', \quad (12)$$

which is verified by substitution. Symmetric solutions of (11) with $\psi(0) = 3$ are also related to the confluent hypergeometric function [22] by $\psi = 3F(-2\alpha, 1/2, -\xi^2/12)$. The resulting similarity profile ϕ is plotted in Fig. 2, using the value of α to be given below.

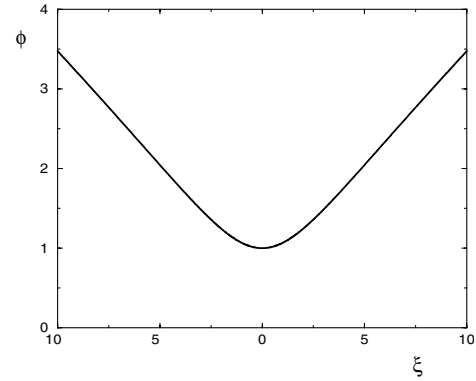


FIG. 2. The symmetric similarity profile ϕ as given by a solution of (11) and (12) with $\alpha = 0.418$.

This gives a complete description of the physical solutions of (10), but one still has to find the value of the exponent α . To that end we compare the weight (6) of solutions with different α , to find the one for which L is minimum. From (8) we find that

$$L = \frac{1}{2D^2} \int_{-\ell}^{\ell} dz a \bar{P} + L_0,$$

where the integration is over the small spatial region where the similarity description applies and L_0 is essentially a constant as $|t'| \rightarrow 0$. The global contribution L_0 depends on the boundary conditions and the position z_0 of the pinch point. For example, in the liquid bridge configuration the filament is much more likely to break in the middle than close to the fixed end points.

Keeping the initial height h_0 of the liquid bridge constant, we find that the integral $\int_0^{t_0} L$ is dominated by contributions from $|t'| \rightarrow 0$ if $\alpha < 1/2$. Thus in similarity variables we have up to constants

$$\int_0^{t_0} dt L = \frac{h_0^2}{2D^2 t_0^{1/2}} \frac{1}{2\alpha - 1/2} \int_{-\infty}^{\infty} d\xi \phi^2 \chi^2. \quad (13)$$

In deriving (13), we have adjusted the free parameter A in $h = A(t_0 - t)^\alpha \phi$, which comes from the scaling freedom, to assure that the initial height h_0 at $t = 0$ is constant. We remark that (13) could also have been used to derive the similarity Eqs. (10) directly. The remaining task is to minimize (13) as a function of α . The decay of the argument of the integral is like $\xi^{4\alpha-4}$, so the integral converges for $\alpha < 3/4$. We conclude that (13) must have a minimum somewhere between $\alpha = 1/4$ and $3/4$.

To find it, one has to do the integral numerically for general α and finds $\alpha_{\min} \approx 0.418 < 1/2$, consistent with the assumptions made above. The typical trajectory of the minimum is thus $h_{\min} = h_0(t_0 - t)^{0.418}$, which corresponds to a *diverging* speed of pinching. In the surface-tension-driven deterministic case, on the other hand, this speed approaches the constant value $0.03\gamma\rho/\nu$ [11]. This means surface tension has become less efficient than thermal

fluctuations in driving the thread towards pinching. We have not yet been able to compute the constant h_0 , which must be determined from matching the similarity solution to a full solution of (8), starting from an appropriate initial profile. The method developed in [20] appears to be an efficient tool to carry out this program, since the the similarity solution (9) could be used as the final profile. Our own numerical simulations based on gathering the statistics of stochastic solutions of (4) and (5) have unfortunately proven quite inefficient.

The speedup driven by fluctuation effects only the last stages of pinching, while the total breakup time is essentially determined by the initial linear growth of disturbances driven by surface tension [8]. From a practical point of view the modifications in the profile shape, which are caused by fluctuations, are of much greater importance. In deterministic pinching, the profile around the pinch point is highly asymmetric [11], forming a drop on one side, while merging into an elongated neck on the other. This invariably leads to the formation of smaller “satellite” drops [23], after the neck has broken off at either end. Without fluctuations, the distribution of drop sizes thus consists of two very sharp peaks, corresponding to main and satellite drops. Since fluctuation-driven pinching is close to symmetric, the breakup typically occurs in the middle between drops of roughly equal size. The resulting single peak in the size distribution will be broadened owing to fluctuations, but the total width of the distribution still *decreases* as a result of fluctuations. This remarkable observation is confirmed by the simulations [10], where the formation of satellites is observed only for some exceptional cases of large fluctuations in the neck region.

In conclusion, we have shown that the path integral method can be used to understand qualitative changes in the behavior of nanoscale flows induced by fluctuations. It seems that this method is particularly well suited to treat problems arising in the new science of nanoscale devices. Typically one is interested in the most probable or typical behavior that brings one to a certain end, say, to have a device complete a given motion. We claim that the present method is tailored to this situation.

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