Dynamics of 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.

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 even larger than in confined geometries. Their importance is estimated by comparing the thermal energy $k_B T$ with the surface tension $\gamma$. Thus for structures whose size is in the order of the thermal length scale $\ell_T = (k_B T / \gamma)^{1/2}$, 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, non-perturbative 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 [4] convincingly showed hydrodynamic behavior on the nanometer scale, and agreement with breakup times and growth rates as predicted by linear theory [2]. Recently [4] a realistic molecular dynamics simulation of a jet of propane issuing from a nozzle 6 nm in diameter was performed, which also payed 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 quasi-stationary decaying state. If nozzles of this size were to be built, this opens dazzling perspectives of transporting current printing and structuring techniques into the nanoworld.

However, a careful analysis of the breakup process revealed [2] 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 [4], noise leads to profiles symmetric around the pinch point. Thus satellite drops rarely form and quite surprisingly the distribution of drop sizes becomes narrower. In addition, on the nanoscale the motion of the minimum neck radius accelerates as breakup is approached, while the corresponding time dependence $h_{\min}(t) = 0.03(\gamma \rho / \nu)(t_0 - t)$ is linear for deterministic pinching [2]. Here $\nu$ is the kinematic viscosity and $\rho$ 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 [1], which consists in adding a stochastic term to the lubrication description of a deterministic jet [2]. The amplitude of the noise is fixed by the condition of detailed balance [2]. 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 [2], reads

\[
\partial_t h^2 + (h^2 v)' = 0 \tag{1}
\]

\[
\partial_t (h^2 v) + (h^2 v^2)' = -G + 3(h^2 v')' + D(h\xi)', \tag{2}
\]

where the prime refers to differentiation with respect to the spatial variable. The first equation (1) expresses mass conservation. $h$ is the momentum balance. All quantities are written in units of the intrinsic length and time scales $\ell_\nu = \nu^2 / \gamma$, $t_\nu = \nu^3 / \gamma^2$, respectively. For later convenience the Laplace pressure term is written in the form $G' = h^2 \kappa'$, $\kappa'$ being the mean curvature of the interface. The Gaussian Langevin force is uncorrelated in space and time,

\[
<\xi(z_1, t_1)\xi(z_2, t_2)> = \delta(z_1 - z_2)\delta(t_1 - t_2), \tag{3}
\]

and the dimensionless constant $D = (6/\pi)\ell_T / \ell_\nu$ 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 $P = \int_0^t p(x) \, dx$, where $p = h^2 v$ is the momentum. Thus we arrive at the conserved form of the equations

\[
\partial_t h^2 = -P'' \tag{4}
\]
\[ \frac{\partial}{\partial t} P = -(P^2/h^2) - G' + 3h^2(P'/h^2) + Dh\xi. \] (5)

Figure 3 shows the collapse of a liquid thread of propane 6mm in diameter as given by [2] 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 pinch-off 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 done 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 pinch-off to have occurred, so the 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 \( \xi \), one finds [3] that the probability for such a path is

\[ W\{h(z,t), P(z,t)\} \sim \exp\left(-\int_{0}^{t_0} dtL\right), \] (6)

where the “Lagrangian” is

\[ L = \frac{1}{2D^2} \int dz \left\{ \dot{P} + (P^2/h^2) + G' - 3h^2(P'/h^2) \right\}^2. \] (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 [13] 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 \( \tilde{P} = \partial L/\partial \dot{P} \) as the conjugate field, in the literature on critical phenomena also known as the “response” field [14,16]. From this one directly finds the Hamiltonian equations

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

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

“Optimal” paths such as those described by (5) have recently enjoyed some popularity in the statistical mechanics literature [13,18]. However, there are two conceptual difficulties associated with (5). 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 [13] 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. 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 (5).

Both problems can simultaneously be dealt with by assuming that the solution is self-similar, as found for the deterministic solution [18,20]. This means we assume solutions for small \( |t'| = |t_0 - t| \) to be of the form
where the exponent $\alpha$ remains to be determined. Plugging (3) into (5), one finds the similarity equations

$$-2\alpha \psi^2 + \frac{\xi}{2} (\phi^2)' = -\psi''$$

$$-2\alpha \psi + \frac{\xi}{2} \psi' = -\psi^2 / \phi^2 + 3 \phi (\psi' / \phi^2)' + \phi^2 \chi$$

$$\Gamma + \frac{\xi}{2} \chi' = -\frac{1}{2} \chi^2 - \chi \psi^2 / \phi^2 - 3 (\chi \psi)' / \phi^2$$

$$\chi + \frac{\xi}{2} \chi' = -2 (\chi \psi' / \phi^2)' - 3 ((\chi \phi^2)' / \phi^2)' + \Gamma''$$

where now the prime refers to differentiation with respect to $\xi$. 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 timescale set by $|t'|$ [1], which means that $|t'|$ must drop out of the similarity description for large arguments $\xi \rightarrow \pm \infty$. For the profile $\phi$ 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 [1]. Amazingly, we found that the subset of solutions of (10) with the correct asymptotic behavior obey the second order linear equation

$$\psi'' = \frac{2\alpha}{3} \psi - \frac{\xi}{6} \psi'$$

and the other functions can be written in terms of $\psi$ as follows:

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

which is verified by substitution. Symmetric solutions of (10) with $\phi(0) = 3$ are also related to the confluent hypergeometric function [2] by $\psi = 3 F (-2\alpha, 1/2, -\xi^2/12)$.

FIG. 2. The symmetric similarity profile $\phi$ as given by a solution of (11) [2] 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 $\alpha$. To that end we compare the weight [3] of solutions with different $\alpha$, to find the one for which $L$ is minimum. From (3) we find that

$$L = \frac{1}{2D^2} \int_0^\xi d\alpha P + L_0,$$

where the integration is over the small spatial region where the similarity description applies and $L_0$ is essentially a constant as $|t'| \rightarrow 0$.

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

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

The remaining task is to minimize (13) as a function of $\alpha$. 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 (3) must have a minimum somewhere between $\alpha = 1/4$ and $3/4$.

To find it, one has to do the integral numerically for general $\alpha$ and finds $\alpha_{min} \approx 0.418 < 1/2$, consistent with the assumptions made above. In particular, $\alpha$ is smaller than 1, so surface tension becomes asymptotically sub-dominant, and hence the singularity is driven by noise alone. A more quantitative comparison with numerical simulations requires considerably better statistics than we are presently able to accumulate.

We have thus shown that the optimal path method can be used to reveal qualitatively new features of nanoscale flows, namely a speed-up in pinching and symmetric profiles. 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. I claim that the present method is tailored to this situation.

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