

Universality Crossover of the Pinch-Off Shape Profiles of Collapsing Liquid Nanobridges in Vacuum and Gaseous Environments

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Liquid propane nanobridges were found through molecular dynamics simulations to exhibit in vacuum a symmetric break-up profile shaped as two cones joined in their apexes. With a surrounding gas of sufficiently high pressure, a long-thread profile develops with an asymmetric shape. The emergence of a long-thread profile, discussed previously for macroscopic fluid structures, originates from the curvature-dependent evaporation-condensation processes of the nanobridge in a surrounding gas. A modified stochastic hydrodynamic description captures the crossover between these universal break-up regimes.

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Generation, stability, and breakup of fluid structures with reduced dimensions (nanoscale jets and bridges) are topics of basic interest due to the unique behavior of liquids at extreme small sizes, as well as fundamental questions pertaining to the applicability of the Navier-Stokes continuum hydrodynamics for liquids miniaturized to the limit of molecular dimensions [1]. Added interest derives from technological considerations in the areas of surface patterning, printing, droplet formation, spraying, and drug delivery [2]. Recently, it has been shown through molecular dynamics (MD) simulations [1] that coherent liquid (propane) jets and bridges, with a diameter as small as 6 nm, can indeed be formed in vacuum and that the stability and break-up processes of these structures close to pinch-off differ radically from those found at larger sizes. In particular, it is commonly observed for larger fluid structures that the break-up profile exhibits an extended thin long thread (LT) with an asymmetric profile of the liquid about the pinching point [3,4] (in agreement with the deterministic lubrication approximation to the Navier-Stokes equations). The LT profile has been shown [4] to be a universal solution (i.e., independent of initial conditions) of the deterministic lubrication equations (LE).

For liquid structures of reduced size, a qualitatively new universal break-up profile, resembling two cones joined at their apexes [called the double-cone (DC) profile] and leading to a symmetric pinch-off, was unveiled through MD simulations [1]. These findings led to the derivation of a stochastic hydrodynamic lubrication equation (called SLE), where size-dependent stress fluctuations are included, that successfully reproduced the simulation results [1]. Subsequent analysis of the SLE confirmed [5] that indeed symmetric pinch-off is the most probable outcome of the SLE and that fluctuations speed up the break-up process, dominating over the effect of surface tension. We remark that the focus here is on the occurrence probabilities of various solutions and, in particular, on finding the most probable solution (when it exists).

Here we discovered through MD simulations of propane nanobridges in a gaseous environment (propane or nitro-

gen) that at sufficiently high partial gas pressure two break-up profiles occur with essentially equal probabilities: One is the aforementioned symmetric, DC, solution (discussed before in the context of a vacuum environment [1]), and the other one is the asymmetric, LT, profile. The reappearance of the LT break-up profile of the nanobridge, caused by the gaseous environment, is particularly surprising, since this universal solution has been discussed previously only for macroscopic liquid systems [3,4]. We find that the microscopic origin of the emergent crossover of universal break-up regimes discussed by us here involves the effect of the surrounding gas on evaporation-condensation processes of the nanobridge. One of the main achievements of this study is the formulation of a modified SLE description (MSLE) where a curvature-dependent term, representing the dependence of the evaporation-condensation flux on the presence of the surrounding gas, is included in the continuity equation. Integration of the newly derived MSLE is shown to yield results that agree well with the MD computer experiments.

The methodology and interaction potentials for propane (C_3H_8) employed in our MD simulations have been described in Ref. [1], and the N_2 intermolecular interaction was chosen after Ref. [6], with a soft spring ($K = 112 \text{ J/m}^2$) connecting the nitrogen atoms. The interaction between the propane and nitrogen molecules was described by a 6–12 Lennard-Jones potential with the potential well depth ϵ and the distance parameter σ , obtained from the Lorentz-Berthelot mixing law [7]. The simulations were performed in a three-dimensional cubical calculational cell with a side length of 30 nm, and an initially cylindrical liquid bridge of length $L = 30 \text{ nm}$ and a radius $h = 3 \text{ nm}$ was placed in the center of the cube; two short cylindrical end caps (made of frozen liquid propane, with the atoms remaining static throughout the MD simulation), each with a diameter of 8 nm and a thickness of 2 nm, were placed at both ends of the bridge. In simulations of a liquid bridge system in vacuum, propane molecules that reach the computational cell boundaries are removed, while when the propane bridge developed in the presence of its own vapor,

the system was closed through the use of reflective boundary conditions at the computational cell boundaries. Similar reflective boundaries were used in simulations of a propane bridge in a nitrogen gas environment, with only the nitrogen molecules confined by the reflective cell boundaries. Prior to the start of the simulation of the dynamic evolution of the bridge, the liquid nanostructure and the ambient gas (when present) were thermalized to a temperature of 185 K, which is below the boiling temperature (230 K) and well above the melting temperature (84 K) of propane. In our simulations, we considered nitrogen densities up to 34.85 kg/m^3 (corresponding pressure of $\sim 1.7 \text{ MPa}$) to avoid condensation.

Fluctuations dominate the break-up behavior of liquid structures [liquid bridges (LB), in particular] whose diameter $d = 2h$ is comparable to the thermal length scale (of the order of a nanometer), determined by the relation between the thermal energy $k_B T$ and the surface tension γ , i.e., $L_T = \sqrt{k_B T / \gamma}$ [1]. In addition, observation of breakup requires that the length of the LB will obey $L > \pi d$, which is the smallest wavelength of a perturbation that leads to instability of the LB [4]; this is satisfied for all of our systems.

We showed first through MD simulations that, for a sufficiently large LB (i.e., initial configuration with $L = 120 \text{ nm}$ and $d = 24 \text{ nm}$, containing over 1.3×10^6 particles), asymmetric LT breakup occurs. This break-up mode is also found by the LE, as well as the SLE, which yields a LT break-up profile with a high probability $P_{LT} = 0.7$.

Reducing the initial diameter of the LB results in the emergence of a new universal break-up density profile. The development of a DC pinch-off profile [1] is illustrated in Fig. 1, through selected configurations taken from MD simulations of a smaller size propane bridge ($L = 30 \text{ nm}$ and $d = 6 \text{ nm}$). In this case, the SLE yielded a DC profile with a probability of $P_{DC} = 0.7$ and $P_{LT} = 0.3$. Furthermore, our simulations revealed that the behavior of the minimal cross section of the neck profile obeys $h_{\min} \sim (t_0 - t)^\alpha$ (where t_0 is the pinch-off time), with $\alpha = 0.40 \pm 0.02$, in agreement with analysis [5] of the SLE that yielded $\alpha = 0.418$; we recall that for macroscopic bridges [8] $\alpha = 1$.

When adding ambient gas (here we use molecular nitrogen) to the bridge system, the shape of the most probable break-up profile changes in a remarkable manner. In these simulations, the density of the gas was increased up to 34.85 kg/m^3 (the density of air under common conditions is about 1.22 kg/m^3). For low ambient gas densities, the DC pinch-off profile maintains. However, when the ambient gas density is increased to above 3.5 kg/m^3 (a corresponding partial pressure of about 0.19 MPa , or about 2 atm), another break-up configuration emerges, characterized by a long thread (Fig. 2), with its probability of occurrence rising to a saturation value $P_{LT} = 0.5$ over a relatively narrow partial pressure range [9]. While for the

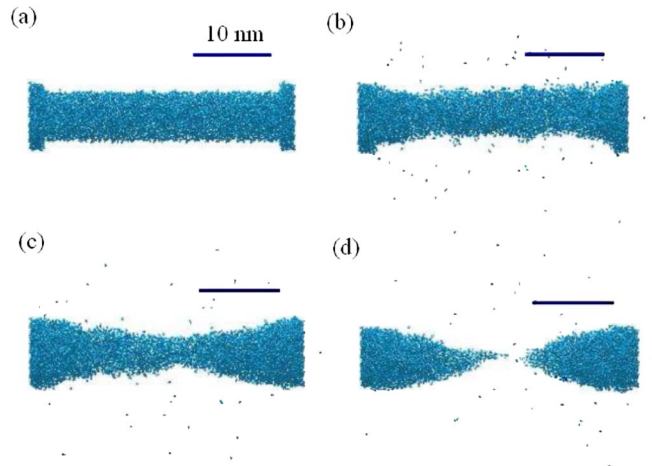


FIG. 1 (color online). A typical break-up process of a propane liquid bridge in vacuum at 185 K, recorded in a MD simulation, at $t = 0$ (a), 200 (b), 400 (c), and 547 ps (d). The break-up profile is shown in (d), exhibiting a geometry of two cones joined at the apex and pinching in the middle. The length of the nanobridge is 30 nm, and its initial average radius is 3 nm. Note also some evaporation of the bridge molecules.

DC configuration the nanobridge pinch-off occurs in the middle of the bridge (and the liquid profile is symmetric), for the new LT pinch-off profile breakup occurs at either end of the bridge (and the profile is asymmetric). We recall that the LT break-up profile is commonly observed for macroscopic systems, and it is indeed the universal solution [4] for the break-up configuration described through

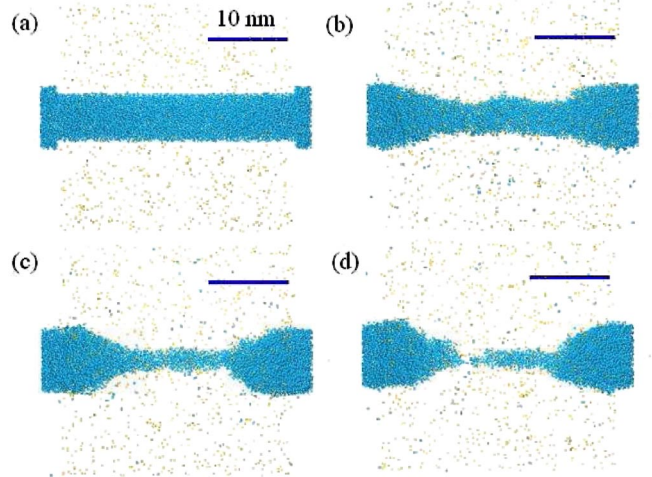


FIG. 2 (color online). A typical break-up process of a propane liquid bridge (blue) at 185 K in an ambient nitrogen gas (yellow) environment (density of 6.0 kg/m^3 , with a corresponding partial pressure of 0.36 MPa), recorded in a MD simulation at $t = 0$ (a), 400 (b), 760 (c), and 840 ps (d). The break-up profile is shown in (d), exhibiting a geometry of a LT pinching on the left. The length of the nanobridge is 30 nm, and its initial average radius is 3 nm.

the LE (sometime called the “slenderness approximation”).

Observation of a new, DC break-up profile in MD simulations of liquid jets and bridges of nanoscale sizes [see Fig. 1 and top panel in Fig. 3(a)] and the failure of the LE to account for the new behavior [see middle panel in Fig. 3(a)] provided the impetus for reformulation of the hydrodynamic equations for systems of reduced dimensions [1]. This led to a derivation of the SLE where size-dependent fluctuations are included. These equations have been shown numerically [1] and analytically [5] to result in symmetric breakup with a DC pinch-off geometry [see bottom panel in Fig. 3(a)] which replaces the LT as the most probable universal break-up profile. In light of these developments, the reemergence of the LT break-up profiles for nanoscale systems (liquid bridges and jets) in the

presence of a surrounding gaseous environment, culminating in asymmetric pinch-off, is rather surprising. Furthermore, we have shown through extensive examination of the spectrum of fluctuations of these systems that the nature of fluctuations (white noise) that characterizes them is essentially indistinguishable from the one found for the same liquid systems in vacuum. Consequently, the reemergence of the LT breakup cannot be attributed to an environmentally induced decreased, or largely modified, contribution of the intrinsic size-dependent fluctuations underlying the SLE hydrodynamic description.

The effect of the environment on the liquid system can be incorporated into the continuum SLE formalism as follows [10,11]. For a segment of the fluid with a local curvature $\kappa(z)$ (with the z axis along the bridge), the vapor pressure inside the liquid $P(z)$, near equilibrium, is given by the following approximation to the Gibbs-Thompson equation: $\Delta P(z)/P_0 = \kappa(z)\gamma v_0/k_B T$, where P_0 is the pressure of the environmental gas (assumed to be ideal) in equilibrium with a planar surface ($\kappa = 0$), $\Delta P(z) = P(z) - P_0$, γ is the surface free energy of the fluid, and v_0 is the volume of a fluid molecule; note that, since the bridge geometry does not cause trapping of the surrounding gas and since the mean-free path in the surrounding gas is sufficiently large, P_0 is essentially constant along the fluid structure. Using the fluid evaporation and condensation fluxes, given by $j_{ev} = P(z)/(2\pi M k_B T)^{1/2}$, where M is the weight of a fluid molecule, with the condensation flux (j_{cond}) given by the same expression but with $P(z)$ replaced by P_0 , we obtain for the net evaporation-condensation flux $j(z) = j_{ev} - j_{cond} = \Delta P(z)/(2\pi M k_B T)^{1/2} = B\kappa(z)$, with $B = P_0\gamma v_0^2/(2\pi M)^{1/2}(k_B T)^{3/2}$. The curvature dependence of the net flux $j(z)$ can now be included in the continuity equation [Eq. (2) below], which together with the SLE [1] velocity equation [Eq. (1) below] gives the MSLE for the velocity $v(z, t)$ and radius $h(z, t)$ of the fluid nanostructure [12],

$$\partial_t v + v \partial_z v = -\frac{\gamma}{\rho} \partial_z \kappa + 3 \frac{\eta}{\rho} \partial_z (h^2 \partial_z v) / h^2 - \frac{1}{\rho} \sqrt{\frac{6k_B T \eta}{\pi}} \partial_z (hN) / h^2, \quad (1)$$

$$\partial_t h + v \partial_z h = -(\partial_z v)h/2 - B\kappa. \quad (2)$$

The curvature is given by $\kappa(z, t) = 1/(h(z, t) \times \{1 + [\partial_z h(z, t)]^2\}^{1/2}) - \partial_z^2 h(z, t) / \{1 + [\partial_z h(z, t)]^2\}^{3/2}$. In Eq. (1), η and ρ are, respectively, the fluid viscosity and density, and N is a standard Gaussian (white) noise [1]. The first term on the right in Eq. (1) contains the partial derivative of the Young-Laplace expression [1] for the pressure in the fluid. The curvature dependence in Eq. (2) represents a redistribution of molecules along the bridge due to evaporation-condensation processes. Such a redistribution, resulting from backscattering of evaporating

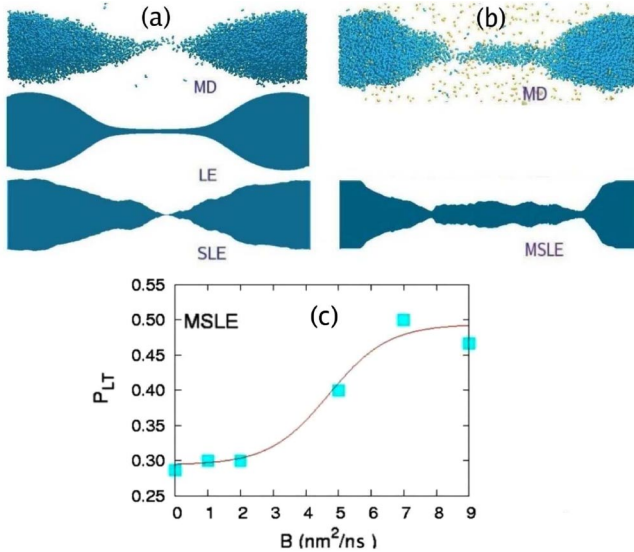


FIG. 3 (color online). (a),(b) Break-up configurations of propane bridges taken from microscopic MD simulations and from continuum hydrodynamic LE [Eqs. (1) and (2) without the last term on the right of Eq. (1) and $B = 0$ in Eq. (2)], SLE [Eqs. (1) and (2) with $B = 0$], and MSLE calculations [Eqs. (1) and (2)]. (c) The occurrence probability of the LT break-up profile for a propane bridge in a N_2 gaseous environment, obtained from solution of the MSLE, for a range of values of the coefficient B in Eq. (2). (a) Top: DC break-up configuration from MD simulations of a propane bridge at 185 K; middle: the LT break-up configuration for the propane bridge obtained from the continuum LE equations; bottom: the DC profile obtained through solution of the SLE equations. (b) Top: The break-up profile exhibiting a LT obtained from MD simulations of the propane bridge in a N_2 gaseous environment described in the caption of Fig. 2; bottom: the LT break-up configuration obtained from solution of the MSLE ($B = 6.9$ nm²/ns). (c) Occurrence probability of the LT break-up profile obtained from solution of the MSLE for selected values of B . Each solid square was calculated from 20 simulations of the MSLE, each with a different random noise sequence. A line fit is added to guide the eye.

molecules due to collisions with gaseous ones, becomes effective for sufficiently high gas pressures; it does not occur in vacuum, and, correspondingly, the curvature-dependent term in Eq. (2) is not included for a nanobridge in vacuum [14].

Direct numerical integration of the above MSLE shows the appearance of a LT break-up profile [see Fig. 3(b), bottom, where it is shown together with a configuration taken from the MD simulation], with the LT occurrence probability P_{LT} increasing for larger values of the coefficient of the curvature-dependent term B in Eq. (2) [see Fig. 3(c)]. The range of values of the coefficient B covered in the MSLE calculations [Fig. 3(c)] coincides with that for which we have performed most of our MD simulations of the nanobridge [13]. As aforementioned, in these MD simulations the LT occurrence probability was found to increase for surrounding gas pressures that are larger than 0.19 MPa (corresponding to $B = 3.63 \text{ nm}^2/\text{ns}$, according to the above expression for B), showing saturation at $P_{LT} = 0.5$ for gas pressures equal to (or larger than) 0.33 MPa, corresponding to $B = 6.3 \text{ nm}^2/\text{ns}$. The agreement between the results of our MD experiments and the hydrodynamic MSLE formulation supports the validity of this continuum approach to nanoscale fluid systems; in addition to the nanobridges discussed here, the MSLE describes also the appearance of a LT break-up profile as the most probable pinch-off mode for nanojets propagating in a gaseous environment.

In summary, we have unveiled here through molecular dynamics simulation experiments a universality crossover of the pinch-off density profile of collapsing liquid propane nanobridges, from a symmetric double-cone shape in vacuum to an asymmetric breakup of a long-thread profile that emerges in a gaseous environment with a sufficiently high pressure. Underlying this phenomenon is the dependence of the evaporation-condensation processes of the nanobridge on the local curvature, when in the presence of a surrounding gas. A modification of the stochastic hydrodynamic equations for liquid nanostructures to include this curvature dependence in the continuity equation, with an amplitude that can be calculated from gas kinetic theory, is shown to faithfully capture the universality crossover of the break-up shape profiles. This extends the applicability of the stochastic hydrodynamic treatment of nanobridges and nanojets [1] beyond vacuum conditions.

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- [11] Alternatives that we considered included: (i) variation of the surface tension of the fluid due to incorporation of gas molecules (nitrogen)—however, this was not found in our simulations—and (ii) surface diffusional currents triggered by collisions of gaseous molecules with the liquid surface. We found that such currents are too small to influence our results.
- [12] In dimensionless form, the coefficient B in Eq. (2) becomes $B_0 = B t_\eta / l_\eta^2 = B(\rho/\eta)$, where $l_\eta = \eta^2/(\rho\gamma)$ and $t_\eta = \eta^3/(\rho\gamma^2)$ are the length and time scale, respectively (see Ref. [1]). Another scale-free parameter appearing in the dimensionless form of Eq. (1) (see Ref. [1]) is $M_l = l_T/l_\eta$. For propane (see [13]), ρ/η equals $1.3 \times 10^{-3} \text{ ns}/\text{nm}^2$, and the crossover from DC to LT profiles occurs for $B_0 = 8.2 \times 10^{-3}$ (corresponding to $B = 6.3 \text{ nm}^2/\text{ns}$ in Fig. 3).
- [13] In the MSLE calculations, we used $\gamma = 0.01 \text{ N/m}$, $\eta = 4.6 \times 10^{-4} \text{ ns}/\text{m}^2$, and $T = 185 \text{ K}$. The size and boundaries of the liquid bridge were the same as in the MD simulations; i.e., prior to the start of the break-up process, the radius of the liquid propane bridge was taken to be 3 nm, and, as in the MD simulation experiments, it is supported on both ends by two short holders of 4 nm radii; these static holders were kept at fixed positions throughout the integration of the MSLE. The MSLE were solved for each B value 20 times with a different random noise seed in each simulation. The probabilities P_{LT} shown in Fig. 3(c) were computed from these calculations. In calculations of the coefficient B [see discussion in the context of Eqs. (1) and (2)], the mass of a propane molecule is $M = 44 \times 1.66 \times 10^{-27} \text{ kg}$, and, in order to account for the reduced density at the surface region of the nanobridge, we assign the propane molecules at that region a volume that is 3 times larger than the molecular volume in bulk liquid propane, $v_0 = 4 \times 10^{-28} \text{ m}^3$.
- [14] We have found in separate simulations that the evaporation flux in an open system consisting of a liquid propane bridge in vacuum is independent of curvature.