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Rayleigh instability at small length scales

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The Rayleigh instability (also called the Plateau-Rayleigh instability) of a nanosized liquid propane thread is investigated using molecular dynamics (MD). The validity of classical predictions at small length scales is verified by comparing the temporal evolution of liquid thread simulated by MD against classical predictions. Previous works have shown that thermal fluctuations become dominant at small length scales. The role and influence of the stochastic nature of thermal fluctuations in determining the instability at small length scale is also investigated. Thermal fluctuations are seen to dominate and accelerate the breakup process only during the last stages of breakup. The simulations also reveal that the breakup profile of nanoscale threads undergo modification due to reorganization of molecules by the evaporation-condensation process.

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I. INTRODUCTION

The stability of a fluid structure of cylindrical geometry was first studied by Savart [1] who discovered that liquid jet breakup is a property of jet dynamics. Plateau experimentally [2] summarized that the instability arose in the jet when the length of the liquid column exceeded the diameter by a factor. He estimated this factor to be in between 3.13 and 3.17. This phenomenon was given an analytical explanation by Rayleigh [3] who explained that small perturbations in the liquid structure are amplified by surface tension. This causes a varicose deformation of the jet column and causes the jet to break into smaller droplets. For certain wavelengths, these perturbations grow exponentially with time and render the system unstable. The behavior of the liquid structure was explained in detail and the factor suggested by Plateau was attributed a value of 3.14, the value of π. Rayleigh showed that the characteristic droplet size scales with the wavelength of the disturbance that caused breakup. It was shown that the wavelength of the fastest growing disturbance is nearly nine times the radius of the jet. The Rayleigh instability thus explains how a cylindrical fluid structure breaks into smaller structures in the process of attempting to reduce its surface tension. Subsequent works [4–6] have significantly contributed to the understanding of macroscopic liquid breakup.

One of the early works [7] that explored the stability of liquid nanoscale threads using MD discovered that the rupture time of these threads were of the same order of magnitude as predicted by Rayleigh [3]. Studies into the rupture phenomenon of liquid threads [8] obtained dominant wave numbers, which are in agreement with the values predicted by the inviscid linear instability theory. However, studies on the breakup behavior of jets of small length scales [9] have shown the emergence of a new breakup profile—the double-cone profile, which results in symmetric pinch off. This phenomenon has been attributed to the domination of thermal fluctuations at small length scales. Thermal fluctuations act as a competing force to the effect of surface tension in causing the breakup of liquid structures at small length scales. Thermal fluctuations were incorporated into lubrication equations to describe the jet dynamics at small length scales. The work by Eggers [10] confirmed by means of a path integral description that the most probable breakup mode had a self-symmetric profile. Experimental investigations [11] determined that thermal fluctuations become predominant in the breakup of low surface tension fluids. Kang and Landman have studied [12] the pinch-off shape profiles for liquid nanobridges and found that the surrounding environment was a crucial factor in determining the dynamics of evolution. This work also highlighted the dominance of thermal fluctuations at small length scales. Studies into the role of thermal fluctuations [13] in the spreading process of viscous drops on solid substrates discovered enhanced spreading rates. This was confirmed by means of MD studies [14], which validated the predictions regarding spreading rates. An innovative workaround to the high computational requirements of MD is to employ a dissipative particle dynamics (DPD) scheme, which coarse models particles as clusters of atoms or molecules. An implementation of the DPD method has been used to study the stability of jets [15] and cylinders [16] of nanoscale dimensions with exceptional success.

The aim of this study is to investigate how good the Rayleigh predictions about the instability of a liquid thread are at length scales where thermal fluctuations are expected to dominate. This is done by comparing Rayleigh predictions against MD simulations of propane threads of nanoscale dimensions. It is interesting to test the accuracy of classical predictions regarding breakup time in the case of breakup processes where thermal fluctuations become a considerable force. The influence of the stochastic thermal fluctuations in the instability at this length scale is also investigated. The influence of the initial configuration on the stability dynamics of the thread is explored. The evolution of the breakup profile is of special interest as it is the easiest means to identify the forces involved in the breakup process.

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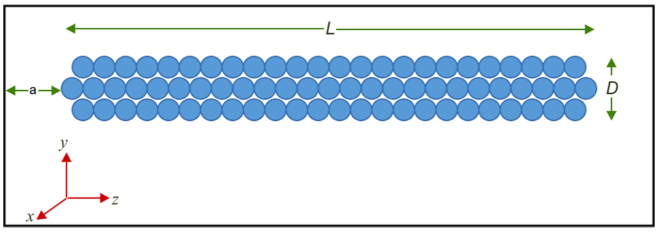


FIG. 1. (Color online) A two-dimensional (2D) representation of the simulation box elucidating the general configuration of molecules in this study. The spheres represent the propane molecules modeled. The figure is not to scale.

II. SIMULATION DETAILS

The simulation box (Fig. 1) consists of a Lennard-Jones (LJ) fluid bridge (parameters chosen to be that of propane [17]) time integrated using a velocity Verlet algorithm with a time step of 1 fs. Three diameters (D) of threads, are simulated: 2.6 nm, 3.9 nm, and 5.2 nm; each for five random seed values and three different lengths (L) (325 nm, 650 nm, and 975 nm) and two temperatures (185 K and 205 K). The summary of the 90 simulations performed are given in Table I. A modified version of the LAMMPS MD package [18] was employed for the simulations and property evaluation was performed by postprocessing the MD trajectory using codes developed in-house. Visualization of MD trajectory was done using OVITO [19]. In order to avoid unnatural interactions between thread ends (due to the periodic boundary condition enforced on the simulation box) a spacing, a, of length 3.25 nm is incorporated between the thread end and the simulation box boundary along the z axis. The size of the simulation box is 26 nm × 26 nm × $L + 2a$ nm in the x, y, and z direction respectively. A 10000 step long equilibration procedure is performed with a Langevin-style thermostat. The selection of the Langevin thermostat was done based on experiences from a previous work [20], which investigated the effects of thermostats in the simulation of nanojets. The Langevin thermostat performs Brownian dynamics on the propane molecules where the total force on each molecule will have the form:

$$f_{\text{total}} = f_c + f_d + f_r, \tag{1}$$

TABLE I. The simulation parameters employed in this study. Viscosity and surface tension were calculated from equilibrium MD simulations.

Parameter	Value
Van der Waals radius, σ	0.466 nm
Well depth, ϵ	0.553 kCal/mole
Friction factor, $\frac{1}{\varphi}$	0.5
Number of molecules	$56561 (D = 2.6\text{ nm}, L = 325\text{ nm})$ to $295601 (D = 5.2\text{ nm}, L = 975\text{ nm})$
Surface tension, γ	1.32×10^{-2} N/m at 185 K
Dynamic viscosity, μ	4.2×10^{-4} Ns/m^2 at 185 K
Time step	1 fs
Equilibration duration	10000 time steps
Thermal length scale, l_T	0.4399 nm at 185 K

where f_c, f_d and f_r are the conservative force, the drag force and the random force acting on the molecule respectively. The conservative force, on account of the Lennard-Jones potential used to model the interaction between propane molecules can be written as

$$f_c = -24\epsilon\left[2\left(\frac{\sigma^{12}}{r^{13}}\right) - \left(\frac{\sigma^6}{r^7}\right)\right]. \tag{2}$$

The drag force is defined as

$$f_d = -\frac{m}{\varphi}v, \tag{3}$$

where m is the mass of the molecule and v is the velocity of the molecule and $\frac{1}{\varphi}$ is the friction factor, which is set to 0.5. The random force is introduced to model the collision of molecules into a particle at any given temperature T. Based on the fluctuation-dissipation theorem,

$$f_r \propto \sqrt{\frac{mk_BT}{\varphi dt}}, \tag{4}$$

where k_B is the Boltzmann constant and dt is the time-step size. Uniform random numbers are used to randomize the magnitude and direction of this force. It is to be noted here that the Langevin thermostat only acts on the system during the equilibration phase and the production run consists of a time evolution of the system as per the microcanonical ensemble. No explicit perturbation is applied on the liquid bridge as the equilibration procedure is seen to result in perturbations to the initial structure, due to the action of thermal fluctuations. In order to estimate the temporal evolution of the thread radius a proper estimation on the liquid-vapor interface is required. A cylindrical coordinate adaptive mesh algorithm has been employed for this purpose. The simulation box is sliced into 2 nm bins along the axis (z axis) of the thread. Each such slice is radially divided into four concentric ring bins of width equal to $0.75^k b/4$ where k is a parameter that is initially set to 0 and b (13 nm) is the half the length of the simulation box in the x and y directions. The densities in each ring region is calculated and if the density of the outermost region is equal to or less than half the density of the innermost region, the concentric binning is repeated after incrementing the value of n by unity. This results in the shrinking of the ring regions and the process is repeated until the density condition is satisfied. As the density of the liquid phase is markedly higher than the vapor phase, the procedure will continue until the outermost bin shrinks to the interface region. Once the interface region has been determined, the radius along the x dimension is determined by defining a sector of angular width 10° symmetrically about the x and the negative x axes. The maximum value of the radius in each sector is estimated and the average of the two values is recorded as the radius of the thread in that slice. The steps are repeated in the y direction and across all the slices to calculate the radius distribution of the thread along its length (z direction). The entire procedure is repeated every 100 time steps so as to calculate the temporal evolution of the radius along the two directions (x and y).

The Rayleigh instability manifests as the evolution of a liquid thread over time magnifies initially insignificant perturbations, which grow to determine its dynamics. In order to estimate if the inviscid assumption is valid in the case of the simulations, the Ohnesorge number has to be evaluated. The Ohnesorge number is defined as $\mathrm{Oh} = \eta\sqrt{1/D\gamma\rho}$. Here, η is the shear viscosity, D is the diameter, γ is the surface tension and ρ is the density of the liquid thread. Provided $\mathrm{Oh} \ll 1$, the effect of viscosity in determining the dynamics of the jet can be safely neglected. To determine whether the inviscid assumption is valid, the viscosity of the liquid must be estimated. In order to estimate the viscosity of liquid propane, separate equilibrium simulations were performed and the results were analyzed using the Green-Kubo method. The shear viscosity is defined as

$$\eta = \frac{V}{k_B T}\int_0^\infty \langle P_{xy}(0)P_{xy}(t)\rangle dt, \tag{5}$$

where V is the volume of the system and P_{xy} are the off-diagonal components of the pressure tensor. To ensure that the simulation box size and random seed values used for velocity initialization had minimal effects on the prediction of viscosity, both these parameters were varied. Four simulations of different number of molecules (256, 2048, 16384, and 131072) each with two different random seed values were performed in order to estimate the viscosity of propane. The analysis of the liquid thread also requires the evaluation of the surface tension. The Guggenheim corresponding-states law with values suggested by Gloor *et al.* [21], based on the test area simulation method (TASM), is used to predict the surface tension of liquid propane. The surface tension of liquid propane at 185 K thus calculated is 0.0132 N/m. This suggests that in all cases studied here, the inviscid approximation is valid and as per the classical theory, the relevant time scale is given by the capillary time scale defined as

$$\tau_c = \sqrt{\rho D^3/\gamma}. \tag{6}$$

III. INSTABILITY OF A LIQUID THREAD

Surface tension is measured as the energy required to increase the surface area of a liquid by a unit of area. Thus, some distortion of the liquid thread surface will change its initial cylindrical shape (assuming that the volume of the cylinder remains largely a constant) and lower the energy of the system. Sinusoidal excitations of the thread about the center line will not reduce the surface energy. If the thread radius is changed, the surface energy is affected. Consider a perturbation of the form

$$R(z,\theta) = R_0 + \epsilon\cos(kz)\cos(m\theta), \tag{7}$$

where R_0 is the initial radius of the thread, k is longitudinal wavelength, and θ is the azimuthal angle. The perturbation can thus be considered a Fourier mode of the initial condition $R(z,\theta)$. The azimuthal modulations result in corrugations of the thread's outermost layer and thus result in increases in surface area, which in turn increase the surface energy. The initial volume of the thread, V_0 is given by

$$V_0 = \pi R_0^2\int_L dz. \tag{8}$$

The volume at any point in time is given by

$$V(t) = \int_L \pi R^2 dz. \tag{9}$$

As the volume is conserved, then $V_0 = V(t) = \text{const.}$ For this condition to be satisfied, the mean radius, $\bar{R}$ should then be of the form

$$\bar{R} = R_0 - \frac{\delta^2}{4R_0}. \tag{10}$$

This means that the the mean radius will be lesser than the unperturbed radius. Now, the exact form of the surface energy can be given as

$$E_S = 2\pi\gamma\int_L R(1+R'^2)^{1/2}dz. \tag{11}$$

The initial surface energy can be expressed as

$$E_0 = 2\pi\gamma R_0\int dz. \tag{12}$$

Consider a cylindrical jet that breaks up into a spherical droplet. If we assume that the volume of the structure is conserved, we can equate the volume of the cylinder with that of the resulting drop,

$$\pi {r_c}^2 L = \tfrac{4}{3}\pi {r_d}^3. \tag{13}$$

Thus,

$$r_d = \sqrt[3]{\frac{3}{4}{r_c}^2 L}. \tag{14}$$

The free energy of the liquid is the result of contributions from the surface tension and the capillary pressure. A liquid thread will form a droplet if the free energy can be reduced. Thus,

$$\Psi_c + \Pi_c \geqslant \Psi_s + \Pi_s, \tag{15}$$

where Ψ_c and Ψ_s are the surface tension contribution to the free energy of the cylinder and the sphere respectively. Similarly, Π_c and Π_s are the capillary pressure contribution to the free energy of the cylinder and the sphere respectively. Then,

$$\Psi_c = 2\pi L r_c\gamma. \tag{16}$$

Similarly,

$$\Psi_s = 4\pi {r_d}^2\gamma. \tag{17}$$

Assuming that the interface of the liquid thread with the surrounding vapor is static and thin, the Laplace-Young equation is valid and thus

$$\Delta p = -\gamma\nabla\cdot\hat{n} = \gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right). \tag{18}$$

Considering the capillary contribution to the free energy for the cylinder,

$$\Pi_c = \gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)V_c = \frac{1}{r_c}\pi {r_c}^2 L\gamma \tag{19}$$

$$\Pi_s = \gamma\left(\frac{1}{R_1}+\frac{1}{R_2}\right)V_s = \frac{8}{3}\pi {r_d}^2\gamma. \tag{20}$$

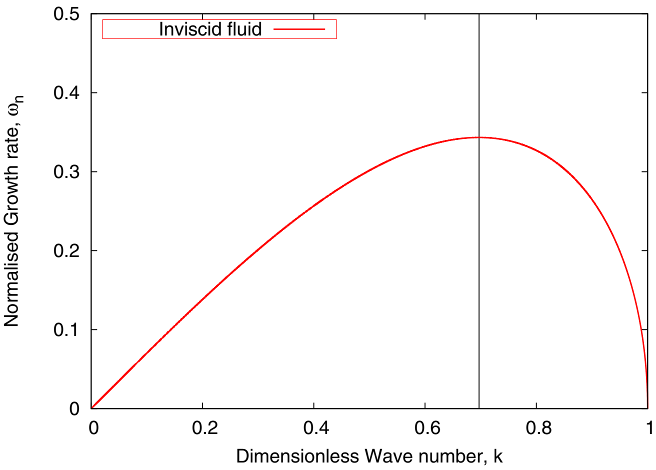


FIG. 2. (Color online) The dimensionless growth rate of sinusoidal perturbations on a cylinder as a function of the wave number, as per Rayleigh's analysis for an inviscid fluid. The maximum growth rate $\omega_{n,\max}$ has a value of 0.3433 corresponding to $k = 0.697$.

Thus,

$$2\pi L r_c\gamma + \gamma\pi r_c L \geqslant \tfrac{8}{3}\pi {r_d}^2\gamma + 4\pi {r_d}^2\gamma, \tag{21}$$

which leads to

$$3r_c L \geqslant \tfrac{20}{3}{r_d}^2. \tag{22}$$

Substituting for r_d from Eq. (14),

$$L \geqslant 1.96\pi r_c. \tag{23}$$

Plateau concluded that for any wavelength, λ that is larger than the perimeter of the thread results in negative energy and are thus unstable. The wavelength is defined as

$$\lambda = \frac{\pi D}{k}. \tag{24}$$

Plateau's analysis did not predict which of all the possible modes is the most unstable or how fast an instability grows. Now, if the perturbations are assumed to be small ($\epsilon \ll 1$), the derivative of radius (R') can be neglected. Then the change in surface energy can be expressed as, $\Delta E = E_S - E_0$. Then,

$$\frac{\Delta E}{E_0} = \frac{\epsilon^2}{4h_0^2}[(kh_0)^2 - 1]. \tag{25}$$

Assuming the perturbations are harmonic waves with fixed longitudinal wavelengths (k), the radius at any time can be expressed as

$$R(z,t) = R_0 + \delta e^{i(kx-\omega t)}. \tag{26}$$

In the above equation, ω is the growth rate of the wave. Rayleigh elegantly summarized (Fig. 2) that for a jet that could be considered inviscid, the balance of inertia and surface tension force leads to

$$\omega^2 = -\frac{\gamma}{\rho {R_0}^3}(kR_0)[1-(kR_0)^2]\frac{I_1(kR_0)}{I_0(kR_0)}. \tag{27}$$

In case the viscosity of the fluid is not negligible, the breakup time t_b of a cylinder due to capillary instabilities can be shown to be [6]

$$t_b = C_1\left(\frac{D\mu}{2\gamma}\frac{1}{1-k^2}\right). \tag{28}$$

In the above equation, C_1 is a constant. Now at a constant temperature, the dynamic viscosity (μ) can be assumed to be a constant and it has been shown that the surface tension of threads decreases linearly with radius [22]. Then,

$$t_b = C\left(\frac{D^2}{1-k^2}\right). \tag{29}$$

Thermal fluctuations are expected to play a dominant part in determining the stability of the liquid thread when the thread dimensions are of the order of the thermal length scale, which is defined as $l_T = \sqrt{(k_B T/\gamma)}$. Based on MD calculations for propane at 185 K, the value of l_T is determined to be 0.4399 nm. Thus thermal fluctuations are expected to be dominant whenever the diameter of the thread is close to this value. All three diameters selected for the simulation are larger than this value. This is done in order to estimate the effect of thermal fluctuations at small length scales, which are, however, at least an order of magnitude larger than the thermal length scale. Then, it can be expected that thermal fluctuations will compete surface tension and inertia force to determine the temporal evolution of the thread.

IV. RESULTS AND DISCUSSIONS

The first step of the analysis involves visualization of the MD trajectories. The temporal evolution of the the simulated nanoscale thread reveals a profile consisting of irregular beads of fluid (Fig. 3). This is in stark contrast to the macroscopic case, where the preferred profile resembles beads of uniform size intermittently connected by long threadlike structures. Although the modified shape at nanoscale can directly be attributed to thermal fluctuations, explaining the irregular size of the fluid beads is trickier. In the macroscopic case, a particular wavelength dominates over all others and grows over time to emerge as the driving force behind breakup. The perturbations caused by thermal fluctuations, owing to their flat power spectral density, can be expected to have various wave numbers simultaneously. This results in perturbations of various wavelengths that grow over time. The visualizations seem to suggest that although many of these wavelengths saturate or die with time, when breakup occurs wavelengths are comparable to one another. This can be attributed to the small radius of the liquid thread, which results in faster breakup and consequently offers lesser time for growth or death of initial disturbances. This would explain the profile consisting of beads of fluid of irregular size. In order to get a clearer picture about breakup, it becomes essential to

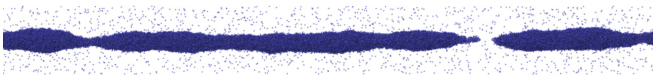


FIG. 3. (Color online) A typical profile obtained during simulation (set 2, 260 ps into the production run). The irregular beadlike fluid structure, which eventually breaks up into pieces of varying sizes, can be seen clearly.

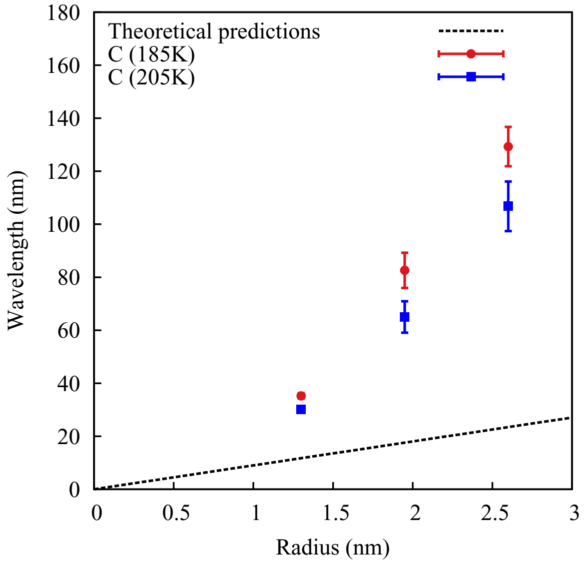


FIG. 4. (Color online) The variation of the effective wavelength as a function of thread radius. Each point is averaged over five simulations with varying random number seeds. The theoretical predictions are obtained from equation (24) with $k = 0.697$.

estimate the effective wavelength of breakup. The parameter referred to as the effective wavelength is calculated as the initial length of the thread divided by the maximum number of pieces into which the thread eventually breaks up. As the pieces have a tendency to roll up into drops and coalesce with one another, tracking the maximum number of drops becomes a challenge. In order to overcome this, for each simulation, the entire MD trajectory is scanned for maximum number of pieces due to breakup. In each simulation, the time at which this occurs is recorded as the breakup time (t_b). It is seen that the effective wavelength calculated is clearly larger than those predicted by Rayleigh (Fig. 4). A casual glance may conclude that this result contradicts the previous study on the breakup time of liquid threads by Koplik and Banavar [7], which reported wavelengths that are an order of magnitude in agreement with Rayleigh theory. Koplik and Banavar [7] focused on the stability of short threads where only a single breakup process was possible. The choice of a shorter geometry for the liquid thread, with only one possible instance of breakup, helps avoid any confusion regarding the definition of a wavelength responsible for breakup. But obviously such a configuration offers no idea if the breakup of a long thread will be caused by a single wavelength. Understanding this difference in configurations is essential to appreciate why the effective wavelength reported in this work is different from the definition of wavelength used by Koplik and Banavar [7]. It is seen that as the radius of the thread increases, the effective wavelength calculated also increases. The simulations reveal that multiple breakups that break the nanoscale liquid thread into drops do not occur simultaneously and are temporally separated. Thus an instance of breakup results in the creation of new free surfaces, which modifies the dynamics of future breakup process. This could explain why the wavelength is larger and consequently the wave number (Table II) is smaller than the Rayleigh predictions. A previous study by Kawano [8] also observed that the wavelengths responsible for breakup are less than 0.697. An increase of temperature is seen to result in greater number of breakups per unit length and thus result in a lower effective wavelength. It must also be emphasized here that faster breakup does not mean simultaneous breakup. Before proceeding any further, an attempt is made to evaluate the correctness of the inviscid assumption. Instead of evaluating

TABLE II. The details of the simulation sets where each set consists of five simulations that vary only in the random seed value used in the Langevin formulation. The mean breakup time denoted refers to the time of first breakup. In case of set 7, only three simulations resulted in breakup.

Set no.	D (nm)	L (nm)	Temperature (K)	Mean breakup time (ps)	Mean number of droplets	Mean wave number, k	C
1	2.6	325	185	138	8.6	0.216	101.167
2	2.6	650	185	137	19.6	0.246	98.956
3	2.6	975	185	213.8	28.6	0.240	94.241
4	3.9	325	185	585	3.4	0.128	295.017
5	3.9	650	185	510	8.6	0.162	254.544
6	3.9	975	185	501	14.6	0.184	248.028
7*	5.2	325	185	1237.5	2	0.101	474.758
8	5.2	650	185	1105	4.8	0.120	423.424
9	5.2	975	185	1069	9.4	0.158	408.506
10	2.6	325	205	110	11.2	0.282	77.730
11	2.6	650	205	113	19.6	0.246	81.456
12	2.6	975	205	94	34	0.285	66.429
13	3.9	325	205	506	4.2	0.158	252.810
14	3.9	650	205	487	10.8	0.204	238.970
15	3.9	975	205	408	16.2	0.204	200.381
16	5.2	325	205	1102	2	0.101	419.560
17	5.2	650	205	1008	6.8	0.171	376.126
18	5.2	975	205	899	11.2	0.188	333.621

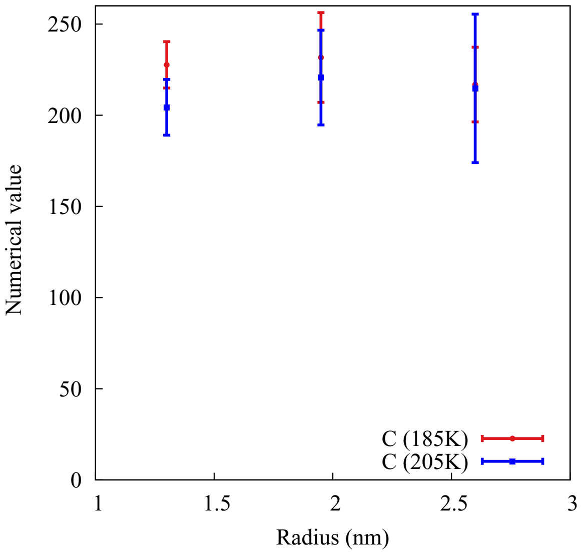


FIG. 5. (Color online) The variation of the constant, C as a function of thread radius. Each point is averaged over five simulations with varying random number seeds.

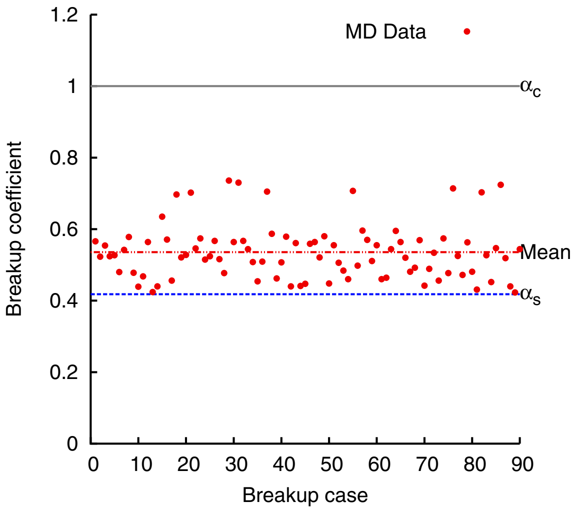


FIG. 6. (Color online) The breakup coefficient (α) calculated for the 90 cases of breakup. α_c refers to the value of α (1) predicted by classical deterministic model while α_s refers to the value of α (0.418) predicted by the stochastic model. The mean value of α obtained from the simulations is found to be nearly 0.536.

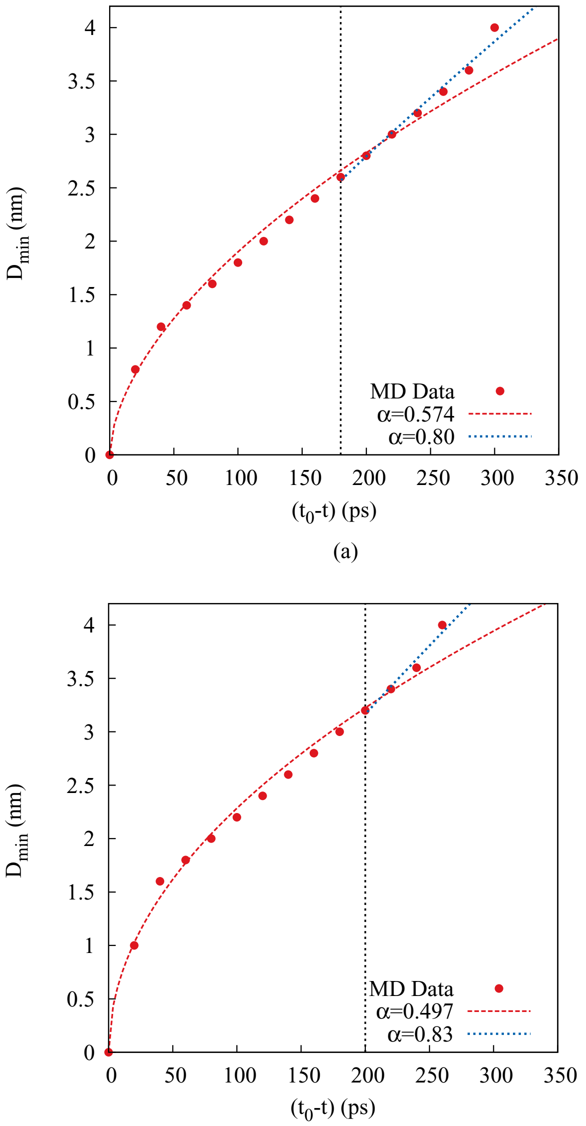
the viscosity using a Green-Kubo approach, an attempt is made to evaluate the viscosity of the liquid thread during the production run. This is done by averaging individual molecular trajectories. It is seen that the viscosity value calculated shows considerable fluctuations (order of 10^2). This can be attributed to the localized fluctuations in fluid density. As the calculation of the effective wave number does not provide a clear insight into the dynamics of breakup the validity of macroscopic scaling laws at this length scale is explored. Following the work of Tiwari *et al.* [16], in order to assess whether the breakup time of a nanoscale liquid thread can be predicted by macroscopic scaling laws, the value of C from Eq. (29) is estimated (Fig. 5). The choice of the viscous equation for predicting breakup time is justified as the validity of the inviscid approximation cannot be established as a fact. It is seen that the value of C obtained for various cases do not show a considerable variation and can be fairly assumed to be a constant. The breakup time predicted by the macroscopic viscid theory thus scales well even into the nanoscale regime. The simulation data suggests that the value of C reduces with increase in temperature. This can be attributed to the fact that changing the temperature of the system changes the values of γ and μ. For simulations at 205 K (cases 10–18), it is noticed that the value of C is lower than for simulations at 185 K (cases 1–9). This can be attributed to the faster breakup of the liquid thread. The effect is very predominant in the comparison of cases 10–12 with cases 1–3. The effect of the increase in temperature is more pronounced in case of threads with smaller radii.

The successful scaling of the macroscopic viscid theory in predicting the breakup at nanoscale and the effect of temperature on breakup raises questions about the nature of breakup at nanoscale. If thermal fluctuations dominate at nanoscale, it seems unlikely that nanoscale breakup can be predicted by scaling down the classical viscid theory. Previous works have attempted to determine whether the nature of breakup is deterministic [23] or stochastic [9]. The time dependence of the minimum diameter ($D_{\min}$) is an excellent indicator of the nature of breakup. The minimum radius depends on time, for both deterministic and stochastic pinching, as

$$D_{\min} \propto (t_0 - t)^{\alpha}, \tag{30}$$

where t_0 is the time at breakup of the liquid structure. In the case of deterministic pinching the time value of α is predicted to be close to 1 [24]. Stochastic pinching on the other hand predicts the value of α to be 0.418 [23]. Thus the value of α serves as a good yardstick to identify the force dominant in determining the stability of the liquid structure. The value of α is obtained by curve fitting the value of $D_{\min}$ obtained from five randomly chosen instances of breakup, from each of the simulation sets (Fig. 6). Only those values of α with a coefficient of determination (R^2) value above 0.95 are chosen.

The variation in the value of α has a mean value of 0.536 thereby establishing that the breakup process at this scale is better described by the stochastic model. It is seen that the breakup profiles are symmetric about the breakup point. The variation from the stochastic prediction (of $\alpha = 0.418$) can be attributed to the spatial resolution of the algorithm implemented. It now becomes necessary to ascertain the contribution of thermal noise to the breakup process. It is evident from the results so far that comparing the thermal length scale with the diameter of the liquid thread is not a reliable means of evaluating the role of fluctuations. In order to do this, two instances of breakup, one corresponding to case 9 and another corresponding to case 18 are compared (Fig. 7). The two threads simulated differ in the initial thermalisation temperature and the initial arrangement of the fluid molecules. The interest of this study is to determine what fraction of the breakup time is dominated by thermal fluctuations and how this varies with temperature. The two cases correspond to the largest initial radius modeled in this study and thus offers a greater chance of detecting



(a)

(b)

FIG. 7. (Color online) The variation of breakup coefficient, α for two cases of breakup. The initial diameter in both cases correspond to 4 nm. The top panel is for simulation at 185 K and the bottom panel for simulation at 205 K. The dotted line in each graph demarcates the surface tension dominant breakup phase.

a surface-tension-dominated breakup regime, if there exists one. It is assumed, in further discussions, that any value $\alpha \geqslant 0.8$ corresponds to a deterministic breakup regime, which is dominated by surface tension.

It is evident from the MD data that the initial reduction of diameter scales closer to the deterministic model rather than the stochastic one. For the sake of comparison, the variation of the diameter for both cases is considered from an initial diameter of 4 nm up to the breakup time when the diameter reaches zero. From the value of α it becomes clear that the thermal fluctuations dominate the breakup process only during its final stages, where an acceleration of the breakup process is quite evident. The total breakup time is in both cases determined by the surface-tension-driven growth of disturbances and thus predictable by a classical viscid theory.

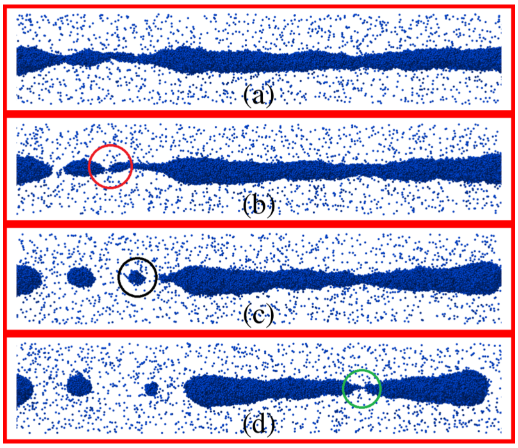


FIG. 8. (Color online) The breakup profile of a simulated nanoscale liquid thread section. The initial diameter is 3.9 nm and length is 975 nm (simulation set no. 9). The rendered images are at (a) 700 ps, (b) 750 ps, (c) 800 ps, and (d) 850 ps, respectively. Both elongated neck and double-cone breakups are observed. In the case of an elongated neck breakup profile, satellite droplet formation is also observed.

It is seen that increasing the temperature decreases the time of breakup. This can be attributed to the reduction of surface tension and the strengthening of thermal fluctuations. Based on our assumption that the breakup process can be considered deterministic if $\alpha \geqslant 0.8$, we see that the breakup process is deterministic 180 ps before t_0 in the case of 185 K and 200 ps before t_0 in the case of 205 K. Clearly, increasing the temperature decreases the duration of the deterministic phase of breakup. Acceleration of breakup in jets as a result of the dominance of thermal fluctuations has been reported by Eggers [10]. Thus, the breakup process in a 4 nm diameter thread is initially driven by surface tension. But as pinching progresses, the thickness of the thread in the necked region drops to few molecular layers. At this stage, thermal fluctuations begin to determine the physics of the breakup process. Although the present study cannot demarcate an exact point at which thermal fluctuations become dominant, the mechanism of breakup is clear with surface tension initiating and driving the initial breakup process and thermal fluctuations accelerating the stages closer to breakup. This effect is detectable only in the case of the larger liquid threads as the surface-tension-dominant breakup phase of smaller threads are too short to detect.

The calculation of the breakup coefficient α also reveals a surprising development—the apparent reemergence of the elongated neck breakup profile, reminiscent of macroscopic liquid thread breakup (Fig. 8). This is surprising as the small thread radius would suggest a thermal-fluctuation-dominated breakup process, leading to symmetric pinch off. This finding is confirmed by means of trajectory visualization of the MD data. Although this seems to contradict the theoretical predictions [10], this phenomenon has been reported in literature [12] and the effect has been attributed to the interaction of the vapor environment with the liquid thread. The interaction results in a net evaporation condensation flux, which in turn leads to a redistribution of the liquid thread molecules. Naturally, this phenomenon is pressure dependent and is more predominant for threads of smaller radii where the redistribution mechanism considerably alters the profile. This is supported by the fact that increasing the initial thermalization temperature from 185 K to 205 K increases the occurrence of this phenomena. It should also be pointed out here that the classical predictions, outlined in the theory, do not account for evaporation-condensation process.

V. CONCLUSIONS

Three-dimensional MD simulations are employed to study the stability of nanoscale liquid threads. It is seen that the nanoscale liquid thread breaks up into pieces of unequal size and the mean wavelength predicted from the number of ruptures is found to be significantly larger than the classical Rayleigh predictions. The profile of the liquid thread is found to resemble irregular sized beads. Based on an understanding of the growth of disturbances in macroscopic liquid threads, this is attributed to multiple waves of comparable wavelength. The classical viscid theory is seen to predict the breakup time of nanoscale liquid threads with surprising accuracy. An analysis of the breakup coefficient, α for various instances of nanoscale thread breakup reveals that the breakup process is closer to stochastic predictions than deterministic ones. It is seen that the breakup process of liquid threads of 4 nm diameter are initially driven by surface tension. Thermal fluctuations dominate only during the last stages of breakup and are seen to accelerate the breakup process. The presence of vapor molecules results in the modification of the breakup profile, which bears resemblance to the classical elongated neck profile.

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