

Coarse Grained Molecular Dynamics Simulations of Sub-Micron Liquid Cylinders and Jets

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Abstract

A coarse-grained molecular dynamics (MD) method, dissipative particle dynamics (DPD), is employed to simulate the breakup of liquid sub-micron liquid cylinders and jets. Consistent with prior findings employing MD, Rayleigh's criterion for capillary breakup of inviscid liquid cylinders is shown to be applicable. Thermal fluctuations are the primary mechanism inducing instability and this leads to the formation of almost monodisperse drops. The parameters varied in the study include the cylinder radius, thermal length scale, viscosity, and surface tension. The breakup time does not show the same scaling dependence as in capillary breakup of liquid cylinders at the macroscale. The time variation of the radius at the point of breakup agrees with prior theoretical predictions from expressions derived with the assumption that thermal fluctuations lead to breakup. The thermal fluctuations accelerate the breakup of liquid jets at the submicron scale. The time evolution of minimum jet radius as given by prior theoretical analysis is recovered.

Introduction

The formation of drops from the breakup of sub-micron scale liquid cylinders and jets is important in many current and emerging applications, such as nanoscale machining, super-fine ink-jet printing, and drug-/gene-delivery to biological cells. The breakup of liquid cylinders and atomization of liquid jets at the macroscale has been a topic of study for over a century [14, 12], but sub-micron scale applications have gained in importance only recently. Computational studies of two-phase flows at the macroscale are complex because of the need to track highly deforming interfaces and develop numerical schemes which can be employed for compressible (gas) and incompressible (liquid) fluids [3]. At the sub-micron scale, the assumption that the fluid properties can be represented by statistical averaging may not hold. At this scale, molecular dynamics (MD) is an obvious choice as a numerical technique [10]. For example, it has been applied to study the behaviour of nanodrops [5] and mixing processes at the nanoscale [8]. Nevertheless, the method is computationally expensive. There are approaches which are computationally less expensive but which sacrifice precise information about dimensions and scales because of lack of adequate information about coarse graining. These approaches are, however, very useful to determine trends in physical behaviour at the sub-micron scale. In this work, the dissipative particle dynamics (DPD) approach will be applied to study the breakup of liquid nanocylinders and nanojets [4,6,7]. An important question here is whether the method can capture the physics associated with sub-micron liquid cylinder and jets.

The Computational Model

The DPD method is particle-based in which each particle represents millions of molecules. The governing equations are written down for the particles and the equations contain quantities which represent the collective behaviour of the millions of molecules they represent. A detailed description of the specific model employed here can be found in Ref. [15].

The position and velocity of a DPD particle i of unit mass are computed from Newton's laws of motion

$$\begin{aligned} \frac{d\mathbf{r}_i}{dt} &= \mathbf{v}_i, \\ \frac{d\mathbf{v}_i}{dt} &= \mathbf{f}_i, \end{aligned} \quad (1)$$

where \mathbf{r}_i , \mathbf{v}_i and \mathbf{f}_i denote the position, velocity and force vectors, respectively. The force has three components: the dissipative force component \mathbf{F}_{ij}^D which is responsible for the viscous effects in the DPD system, the random force \mathbf{F}_{ij}^R which compensates for the lost degrees of freedom from coarse-graining, and the conservative force \mathbf{F}_{ij}^C which accounts for the configurational energy of the DPD system. These forces maintain an isothermal system. The functional forms of the inter-particle forces between particles i and j are given by

$$\begin{aligned} \mathbf{F}_{ij}^D &= -\gamma\omega^D(r_{ij})(\mathbf{e}_{ij} \bullet \mathbf{v}_{ij})\mathbf{e}_{ij}, \\ \mathbf{F}_{ij}^R &= \sigma\omega^R(r_{ij})\xi_{ij}\mathbf{e}_{ij}, \text{ and} \\ \mathbf{F}_{ij}^C &= -\frac{\partial\psi(r_{ij})}{\partial r_{ij}}\mathbf{e}_{ij}. \end{aligned} \quad (2)$$

Here, \mathbf{e}_{ij} is a unit vector given by $\mathbf{e}_{ij} = \mathbf{r}_{ij}/|\mathbf{r}_{ij}|$, where $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$, γ is the amplitude of the dissipative force, σ is the amplitude of random force, ω^D and ω^R are the weight functions for the dissipative and random force, respectively, and ψ is the free energy per particle. Since DPD is a short-range model, the weight functions are chosen such that their values go to zero beyond the cut-off distance, i.e., each particle interacts only with particles which are within the cut-off distance. The term ξ_{ij} in Eq. (4) is a random variable which has zero mean, unit variance, and is uncorrelated in time. It follows Gaussian statistics.

The application of the fluctuation-dissipation theorem to the DPD system gives the following relationship between the amplitudes and the weight functions of the dissipative and random forces [4]:

$$\omega^D(r) = [\omega^R(r)]^2, \sigma^2 = 2\gamma k_B T. \quad (3)$$

In this work, the following functional form for the weight functions in the expressions for the dissipative and random forces have been chosen:

$$\omega^D(r) = [\omega^R(r)]^2 = \begin{cases} (1 - \frac{r}{r_c})^2, & (r < r_c) \\ 0, & (r \geq r_c) \end{cases}. \quad (4)$$

These weight functions depend on the inter-particle separation r and the cut-off radius r_c .

The inter-molecular forces between liquid-liquid molecules, gas-gas molecules and liquid-gas molecules are different. The differences give rise to phase segregation and the macroscopic property of surface tension. In this work, the mean-field theory-based model of Tiwari and Abraham [15] is used. The conservative force \mathbf{F}^C is expressed as

$$\mathbf{F}^C = -\nabla \psi_{non-ideal} + \kappa \nabla \nabla^2 \rho, \quad (5)$$

where $\psi_{non-ideal}$ denotes the non-ideal part of the free energy, ρ is the density, and κ is a model parameter that controls the strength of surface tension; it is related to the second moment of the attractive part of interaction potential between atoms/molecules. In Eq. (5) the first term is responsible for phase segregation and the second for surface tension. The expression for free energy is derived from the van der Waals equation of state

$$p = \frac{\rho k_B T}{1 - b\rho} - a\rho^2, \quad (6)$$

where p denotes the pressure, ρ the density, k_B the Boltzmann constant, T the temperature, and a and b are parameters of the equation of state which are related to the zeroth-moment of the attractive part of the interaction potential and the exclusion volume effects, respectively.

We see from Eq. (5) that the surface tension term depends on the gradients of density. The density ρ in the vicinity of particle i is calculated using the following expression

$$\rho_i = \sum_{j=1}^N w(r_{ij}), \quad (7)$$

where w denotes the normalized weight function, j denotes a particle tag, r denotes the separation, and N denotes the total number of particles. We choose the Lucy weight function given by

$$w(r, r_c) = \begin{cases} c \left(1 + \frac{3r}{r_c}\right) \left(1 - \frac{r}{r_c}\right)^3 & \text{if } r < r_c, \\ 0 & \text{if } r > r_c \end{cases}, \quad (8)$$

where r denotes the inter-particle separation, r_c denotes the cut-off radius and c denotes the normalization constant which has a value $5/\pi r_c^2$ for two-dimensions and $105/16\pi r_c^3$ for three-dimensions. Using the definition of density in Eq. (7) and substituting the free energy obtained from Eq. (6) into Eq. (5), the final form of the inter-particle conservative force is obtained as

$$\mathbf{F}_{ij}^C = \left[- \left\{ \left(\frac{bk_B T}{1 - b\rho_i} - a \right) + \left(\frac{bk_B T}{1 - b\rho_j} - a \right) \right\} w_{ij}^{(1)} + \kappa w_{ij}^{(3)} \right] \mathbf{e}_{ij}, \quad (9)$$

where $W_{ij}^{(1)}$ and $W_{ij}^{(3)}$ denote the first and third derivatives of the weight function in Eq. (8) with respect to the interparticle separation. The parameters that are required for specifying the interparticle conservative force are a , b , κ , r_c and $k_B T$.

The DPD equations of motion are integrated using the following modified-Verlet scheme by Groot and Warren [6]:

$$\begin{aligned} \mathbf{r}_i(t + \delta t) &= \mathbf{r}_i(t) + \delta t \mathbf{v}_i(t) + \frac{1}{2} (\delta t)^2 \mathbf{f}_i(t), \\ \tilde{\mathbf{v}}_i(t + \delta t) &= \mathbf{v}_i(t) + \lambda \delta t \mathbf{f}_i(t), \\ \mathbf{f}_i(t + \delta t) &= \mathbf{f}_i(\mathbf{r}(t + \delta t), \tilde{\mathbf{v}}(t + \delta t)), \\ \mathbf{v}_i(t + \delta t) &= \mathbf{v}_i(t) + \frac{1}{2} \delta t (\mathbf{f}_i(t) + \mathbf{f}_i(t + \delta t)), \end{aligned} \quad (10)$$

where \mathbf{r} , \mathbf{v} and \mathbf{f} denote the position, velocity and force vectors, respectively, t denotes the time, i denotes a particle tag, and λ denotes an empirical parameter. The quantity $\tilde{\mathbf{v}}$ is a guessed value of the velocity. This guess is necessary because the force depends on velocity as seen from the third line in Eq. (10).

Results and Discussion

When the breakup occurs at the sub-micron scale, thermal fluctuations induced as a result of the thermal energy possessed by atoms/molecules can play a dominant role in the breakup process in addition to the classical mechanisms which arise from an imbalance of surface tension forces and internal and external pressure forces. In fact, these thermal fluctuations can accentuate the classical mechanisms. To characterize the influence of thermal fluctuations, a thermal length scale l_T can be defined as

$$l_T = \sqrt{\frac{k_B T}{\sigma_s}}, \quad (11)$$

where k_B denotes the Boltzmann constant, T the temperature, and σ_s the surface tension. This length scale may be compared to a physical length scale such as the radius of the liquid cylinder.

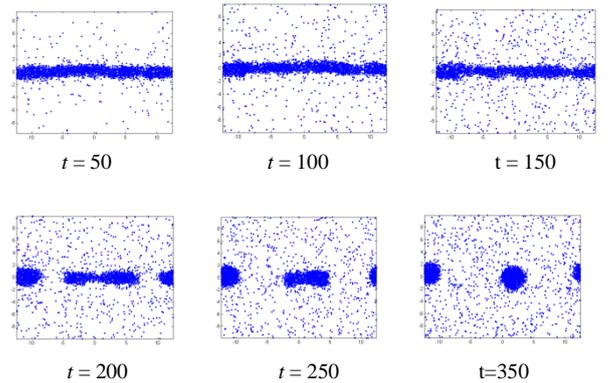


Figure 1. Evolution of instabilities in a liquid nanocylinder leading to breakup.

The computational domain consists of a three-dimensional box with periodic boundary conditions in all three directions. A liquid cylinder is initially positioned as shown in Fig. 1. The liquid to gas density ratio is about 100. The initial arrangement for the particles is a uniform cubic arrangement. Other parameters employed for simulation of nanocylinders and nanojets are given in Table 1.

As the computations proceed, the particles fill the chamber to achieve a liquid-vapor distribution corresponding to the selected state point. It is useful to consider a non-dimensional wave number

$$k = \frac{2\pi r}{\lambda}, \quad (12)$$

where λ is the wavelength of the disturbance. The maximum possible value of λ is the axial length of the domain. Based on Rayleigh's criterion [11], when k is less than 1, instabilities lead to cylinder breakup as multiple modes of instability are captured. In fact, this criterion is met by the simulations. The origin of the instabilities is, however, thermal fluctuations, i.e. molecular in nature. The consequence of this is twofold: first, the drops that are generated are close to monodisperse whereas in macroscale Rayleigh breakup, the drops are polydisperse; second, the time-dependent behaviour of the break-up process is different from that at the macroscale.

Parameter	Value in DPD units
$k_B T$	1.6×10^{-2}
Mean-field critical temperature	3.57×10^{-3}
a (van der Waals parameter)	3.012×10^{-3}
b (van der Waals parameter)	2.5×10^{-2}
σ	1.3×10^{-1}
\mathcal{K}	1.0×10^{-3}
Time step δt	1.0×10^{-2}
r_c	1.05
g (Body force)	7.5×10^{-3}
N	50000
Re	0.86

Table 1. Parameter for simulations (some of the parameters are applicable only for nanocylinders)

The breakup time T_b of a cylinder arising from capillary instabilities has been shown to be [2]

$$T_b = C_1 \sqrt{\frac{r^3 \rho_l I_0(k)}{\sigma_s I_1(k) k(1-k^2)}}, \quad (13)$$

$$T_b = C_2 \left(\frac{r \mu_l}{\sigma_s (1-k^2)} \right), \quad (14)$$

where μ_l is the dynamic viscosity, ρ_l is the density, σ_s is the surface tension, r is the radius of the cylinder, k is the non-dimensional wave-number, and $I_0(k)$ and $I_1(k)$ are modified Bessel functions. Equation (13) is applicable when viscosity is neglected, and Eq. (14) when viscosity is included, for capillary breakup of liquid cylinders at the macroscale. These equations have been shown not to hold at the nanoscale [3]. Also, from linear instability theory [2,9] it can be shown that

$$\eta = \varepsilon e^{\xi t}, \quad (15)$$

where η is the displacement of the interface, ε is the amplitude of the disturbance, ξ is the growth rate, and t is the time. For thermally-induced breakup, ε is a function of the temperature of the system and, say, is proportional to the thermal length scale l_T . Another difference is related to the minimum radius of the breakup point r_{min} . At the macroscale [1, 13]:

$$r_{min} = r_0 (T - t), \quad (16)$$

where r_0 is a constant, T denotes the breakup time and t the current time. When thermal fluctuations play a dominant role, they tend to accelerate the breakup process. Eggers [3] has shown

that the following relationship then holds for the minimum radius r_{min} :

$$r_{min} = r_1 (T - t)^{0.418}, \quad (17)$$

where r_1 is a constant and other symbols have the same meaning as in Eq. (1). The DPD simulations follow this trend quite well as shown in Fig. 2

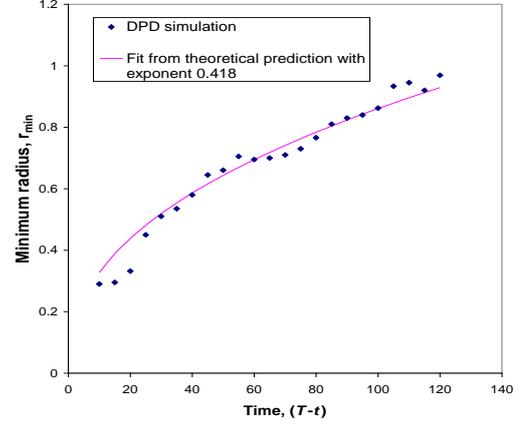


Figure 2. Computed and analytical fit of cylinder radius as a function of $(T_b - t)$.

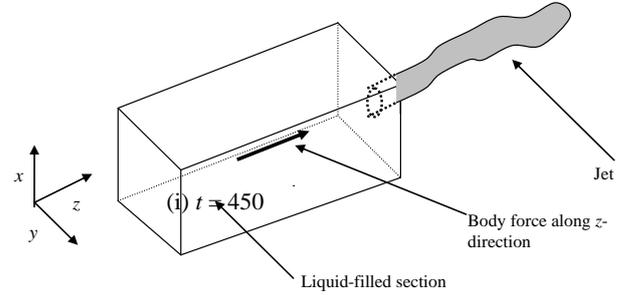


Figure 3. Computational setup

Liquid nanojets have also been the subject of study in recent years both analytically [3] and using molecular dynamics [10]. The essential physics that is discussed above for liquid nanocylinders also holds for nanojets. Figure 3 shows the computational setup for the DPD nanojet simulations. Liquid is initially confined in the syringe shown. A body force acts on the particles in the syringe and causes them to move. While this depletes the number of particles in the syringe, the constant body force acting on the particles forces them to exit with an almost constant injection velocity. The walls of the syringe have frozen particles and the attractive component of the conservative force is removed so that the entry of particles into the wall will be limited. Removal of the attractive component of the force also prevents the liquid particles from sticking to the wall when injected.

Figure 4 shows the time evolution of a liquid nanojet. Thermal fluctuations initiate instabilities. These instabilities lead to a thinning of the jet and breakup. Breakup occurs in regions where symmetric double-cone structures form. The elongated neck which is observed in macroscopic breakup of liquid jets is not present here. As a result, satellite drops do not form.

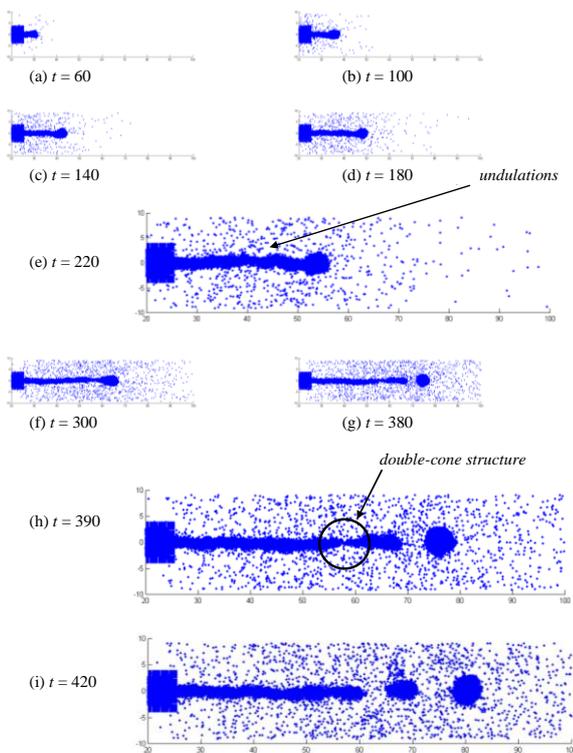


Figure 4. Computed liquid nanojets

Conclusions

Molecular dynamics has been shown to be a powerful tool for studying the physics of fluids at the sub-micron scale. In this paper, it is shown that the coarse-grained molecular dynamics simulation method, dissipative particle dynamics, can also be employed to study the physics at the sub-micron scale. The physics of liquid breakup at the small scale differ from that at the macro scale in significant ways. Breakup is accelerated by the role that thermal fluctuations increasingly play as the scale is decreased. Nevertheless, the Rayleigh breakup criterion holds for the scales considered here. It appears that once the instabilities are initiated, the subsequent physics of wave growth remains similar to that at the macroscale. Breakup occurs symmetrically, i.e. no satellite drops are formed. Hence, the drops are generally monodisperse whereas they are polydisperse in macroscale breakup.

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