A Langevin dynamics study of nanojets

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A R T I C L E   I N F O

A B S T R A C T

The behaviour of nano-scale jets emanating from a reservoir under the action of an external force is studied using Langevin dynamics simulations. The advantage of employing a Langevin thermostat to maintain the temperature of the fluid reservoir is highlighted. The effect of hydrodynamic screening introduced by the Langevin thermostat is considered. It is seen that the nature of thermostat plays a crucial role in simulating the onset of instabilities in the liquid structures. A plunger action has been chosen to initiate jet generation. Langevin dynamics is seen to be able to model the physics of nano-scale jets quite accurately. The study also shows that the Langevin dynamics simulations are capable of capturing the dynamics of nano-scale liquid jets, as the nanojet simulated by this method is found to behave in close agreement with the theoretical predictions for nano-scale jets.

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1. Introduction

The stability of macroscopic liquid structures [1–3] is a topic that has received considerable attention from the scientific community. The stability of liquid structures at small length scales is interesting because of the tremendous potential it holds in revolutionising areas such as drug delivery [4], biological cell structure estimation [5], electronic cooling [6], nano-scale printing [7,8], and nano-scale machining [9]. The study of stability at the nano-scale is challenging because of the emergence of thermal fluctuations as a comparable force to surface tension, viscosity and inertia. The stochastic nature of thermal fluctuations complicates stability analysis at small length scales. Thus, understanding nano-scale fluid stability presents both immense opportunities and considerable challenges. The high spatial and temporal resolution requirements of nano-scale domains make molecular dynamics (MD) [10] an excellent tool for studying structures such as jets, drops and threads. MD studies on the breakup behaviour of jets of small length scales [11] 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 are expected to act as a competing force to the effect of surface tension in causing the breakup of liquid structures at small length scales. The effect of thermal fluctuations was incorporated into lubrication equations to describe the jet dynamics at small length scales. Further work by Eggers [12] confirmed by means of a path integral description that the most probable breakup mode had a self symmetric profile. Kang and Landman have studied [13], using MD, the pinch off shape profiles for liquid nanobridges and found that the

surrounding environment was a crucial factor in determining the dynamics of evolution. The non-equilibrium MD study performed by Chi-Fu Dai and Rong-Yeu Chang [14] investigated the formation of nano-scale droplets and liquid thread breakup of propane in piezoelectric nano-ejection process. Earlier the same group [15] had investigated the dynamics of nano-ejection using MD simulations. Employing MD imposes hydrodynamic time and length scale restrictions on the simulations. To overcome this, Tiwari and Abraham [16] have employed a Dissipative Particle Dynamics (DPD) scheme to analyse the dynamics of nanojets.

When employing MD for studying non-equilibrium phenomena at constant temperature, the choice of a temperature control strategy becomes crucial in capturing the physics involved. Although the application of a thermostat does introduce ersatz conditions such as the instantaneous removal of heat, it allows for a physically meaningful condition of constant temperature. Based on the group on which actual temperature control takes place, thermostats can be classified as either ensemble or particle thermostats. The ensemble thermostat controls the temperature of a group of particles, while the particle thermostat controls the temperature of individual particles (atoms or molecules) in the simulation. Although computationally less taxing, ensemble thermostats tend to 'kill' any secondary flow and effects like thermal fluctuations. This manifests as non-physical behaviour [17] of the simulation system. Workarounds like the Profile Unbiased Thermostat (PUT) [18] which make no *a priori* assumptions about the velocity profile have been suggested.

Another option is to employ a particle thermostat, such as a Langevin thermostat, which thermostats particles individually. The selection of a Langevin style thermostat presents certain advantages. The time discretization of Langevin model has been shown to reproduce the statistical energy distribution for larger time-steps, provided they are

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within the numerical stability limit. One such time-discretization scheme [19] takes the random force at any time-step to be composed of two force components from the previous and present time intervals. Thus the simulation time-step can be increased, thereby increasing the total time of the production run. In a Langevin thermostat, the introduction of the viscous damping force and the random force from fluctuation–dissipation theorem also enables the sampling of the canonical ensemble. The ability to impart different drag forces to different types of molecules, based on their mass, also position the Langevin style thermostat favourably. However, the Langevin thermostat also introduces its own shortcomings into modelling. The major disadvantage of a Langevin formulation would be the loss of momentum transfer information. This is due to the introduction of the random forces. Thus a Langevin thermostat would not be advisable in a situation where calculating the diffusion coefficients would be a necessity. In addition, the Langevin thermostat does not preserve the Galilean invariance of the system being studied, the effect of which will be discussed in further detail.

In the present work, molecular dynamics simulations are performed by time integrating Langevin-like equations using a velocity-Verlet algorithm. The MD simulations employ the Langevin formulation as a particle thermostat in studying the time evolution of jets emanating from a nano-sized opening, under the action of an external plunger. The interest of these simulations is to evaluate the Langevin thermostats' capability of capturing hydrodynamic instabilities in the simulated nanojet. From a simulation perspective, nano-scale jets are an interesting scenario where hydrodynamic forces and thermal fluctuations are equally significant.

2. Simulation details

The 3D simulation box consists of 45,494 molecules of propane equilibrated between 2 slabs of gold each having 13,750 molecules as shown in Fig. 1. The simulation box also has a vacuum region into which the jet is free to expand. The simulation box is periodic in the x and y directions. The simulation box is non-periodic in the z directions and propane molecules are free to move out of the simulation box in this direction. The parameters for the LJ potential are chosen from a previous study [20] and are as given in Table 1. The slabs of gold atoms, which constitute the front and back panels are fixed as rigid and the propane molecules are time integrated using a velocity-Verlet algorithm with a time step of 1 fs. The system temperature is set at 303 K which corresponds to liquid phase. An initial 50,000 step long equilibration is performed with the nozzle closed and a Langevin style thermostat acting on all the propane molecules. The equilibration phase is followed by a 25,000 step long NVE run where the pressure, energy and the temperature of the propane molecules are monitored. Once these values are found to stabilise and fluctuate about statistical mean, the system is assumed to be equilibrated. Atoms within the cylindrical region that constitute the nozzle opening are then deleted and the

Table 1
The Lennard-Jones (LJ) parameters for the interactions in the simulation. The gold–propane interaction parameters have been calculated using the Lorentz–Berthelot mixing rules.

Interaction type	van der Waal's radius, σ	Well depth, ϵ
	nm	kcal mol^{-1}
Gold–gold	0.293	0.039
Propane–propane	0.466	0.553
Gold–propane	0.3795	0.147

position of the remaining atoms of the front panel is fixed in space. The simulations are performed for production runs that last for 1,500,000 time steps or ejection of 90% of the molecules from the nozzle, whichever occurs earlier. At the beginning of the production run, atoms are removed from the front panel so as to form a nozzle for the ejection process. In this study, two circular nozzles of 2.856 and 5.712 nm are studied. The back panel (the plunger) is free to move, thereby compressing the propane molecules between the front panel and itself. In all the simulations that are performed as part of this study, the back plunger is pushed with a force in the z direction. The force is applied such that the net force acting on the atoms that constitute the plunger is 34.7 pN. At each time-step, the total force on the plunger is calculated as the net resultant force of its constituent atoms. The position coordinates and velocities of the plunger atoms are time integrated so that the plunger moves as a single entity. The force is transferred to the propane molecules by means of the gold–propane interaction. The magnitude of the external force was chosen based on the experiences from a previous work [21] which investigated the effects of ensemble thermostats in nanojet generation. During the production run, Langevin thermostat acts only on those molecules which are within a distance of 10.2 nm (along the z direction) from the nozzle opening. The choice of this value was based on density calculations so as to minimise the effect of hydrodynamic screening. The details of this are presented in the Theory section. Furthermore, by limiting the thermostat action to a region, the momentum loss from the plunger to the propane molecules is limited. The simulations were performed by modifying the LAMMPS molecular modelling package [22] and the visualisations were performed using the OVITO visualisation tool [23]. The volume into which the fluid structure evolves is spatially divided, along the z axis, into 1000 bins and the density of the propane molecules in these bins is constantly monitored. This is to estimate the temporal evolution of the nanojet length. In order to estimate the temporal evolution of the jet radius a proper estimation on the liquid–vapour interface is required. A cylindrical co-ordinate 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 jet. Each such slice is radially divided, as shown in Fig. 2, into four concentric ring bins of width equal to $0.75^k a/4$ where k is a parameter that is initially set to 0 and a (5.1 nm) is the half the length of the simulation box in the x and y directions. The densities in
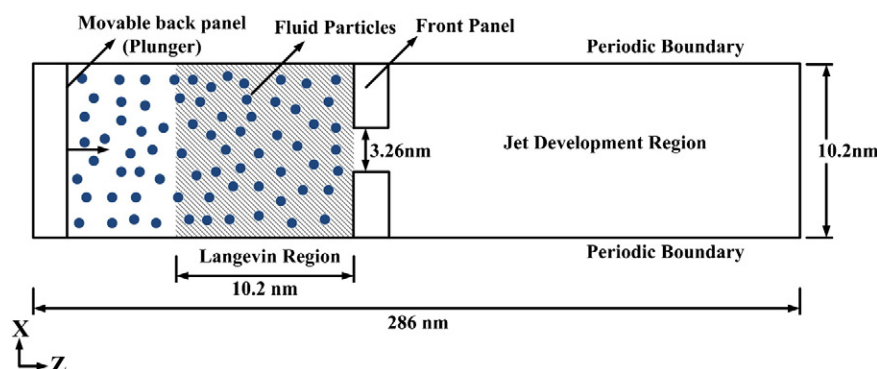

Fig. 1. A 2D schematic of the simulation box. Image not to scale.