

Nanodroplet impact on liquid substrates via molecular dynamics

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ABSTRACT

This paper analyses several aspects of the dynamic behaviour of liquid nanodroplets impacting on liquid substrates using molecular dynamics (MD) computer simulations. We consider nanometer-sized liquid droplets interacting via the Lennard-Jones potential. We simulate their impulsively accelerated movement and their splashing on a liquid layer with the same interactions at various velocities. As the droplet approaches the surface noticeable bridging is observed. The impact creates a deep crater and leads to droplet absorption before the layer's smoothing.

Keywords: nanodroplet, impact, molecular dynamics, liquid substrate/layer, splashing

1 INTRODUCTION

The impact of droplets on liquid surfaces has been studied extensively as a phenomenon of great physical interest that plays an important role in many technological applications. Following the experimental characterisation of the process (for both deep and shallow liquid substrates), when a droplet impacts on a liquid surface, one of the following qualitative behaviours may occur [1-3]: floating, bouncing, coalescence, or splashing. Other aspects of impact may include the formation of a rapidly moving crown from the impact zone, the development of a rising jet from the centre of the impact zone, bubble entrainment and vortex sheet development in the liquid below the impact zone.

Although significant theoretical and numerical work has been done for macroscopic droplet impacts, the results obtained are not necessarily transferable into the nanometer scale as the length scale of the impact itself begins to approach that of the liquid's constituent molecules. However, an array of appealing and challenging technological applications involve spraying of liquids on liquid substrates. Therefore, detailed study and analysis of the prevailing physical mechanisms that, ultimately, control such processes becomes a critical issue.

A significant amount of literature already exists in the general area of nanodroplet physics. For instance, Consolini et al. [4] studied the nanodroplet evaporation, Arcidiacono et al. [5] the oscillatory behaviour of nanodroplets, Murad and Law [6] the mutual collision of nanodroplets, and Gentner et al. [7] nanodroplet impacts on solid surfaces.

More general reviews of the field are given by Poulikakos et al. [8] and Koplik and Banavar [9].

To date, it seems that there has been limited attention on analysing the dynamics of 3-dimensional nanodroplet impacts onto liquid layers. However, developing an understanding of the basic physical mechanisms that govern such processes will provide valuable insights for improving nano-scale aspects in a multitude of challenging technological applications including micro/nano-fabrication, energy generation, pollution control, drug delivery, medical diagnostics, etc.

In view of the above, in this paper several aspects of the dynamic behaviour of liquid nanodroplets impacting on liquid substrates are investigated using molecular dynamics (MD) computer simulations. We consider liquid droplets of 5 nm in diameter, consisting of 7,000 atoms interacting via the Lennard-Jones potential. We simulate the impulsively accelerated movement of such droplets and their splashing on a liquid layer with the same interactions, studying the effects of the impact at various velocities. Section 2 describes the main characteristics of the methodology used. This is followed by Section 3 that presents the results of our simulations, which are then analysed and discussed in Section 4.

2 MOLECULAR DYNAMICS METHODOLOGY

We consider a system of a liquid droplet interacting with a liquid substrate at the nanometer scale. The system consists of N atoms that are assumed to interact via two-body forces described by the 12-6 Lennard-Jones (LJ) potential which provides strong repulsion at short distances and attraction at larger separations [10]:

$$V(r) = 4\epsilon \left[\left(\frac{r}{\sigma} \right)^{-12} - \left(\frac{r}{\sigma} \right)^{-6} \right] \quad (1)$$

where r is the distance between any two atoms. The parameters σ and ϵ represent the diameter of the repulsive core and the depth of the potential energy well, respectively. The inter-atomic force associated with an atom pair is calculated from the negative gradient of the potential. The summation of all inter-atomic forces on an atom leads to the equation of motion for the system according to Newton's law:

$$m \frac{d^2 \vec{r}_i}{dt^2} = -\nabla V(\vec{r}_i), \quad i = 1, \dots, N \quad (2)$$

$$\nabla V(\vec{r}_i) = \sum_{j=1}^N \nabla V(|\vec{r}_i - \vec{r}_j|), \quad i = 1, \dots, N \quad (3)$$

where m is the mass of the molecule. The numerical integration of (2) tracks the trajectory of atoms in the system over time. Within the NVE ensemble, we employ the Verlet leap-frog integrator to update the position and velocity, v , of the atoms for specified timesteps δt [10]:

$$r(t + \delta t) = r(t) + \delta t v(t) + \frac{1}{2} \delta t^2 a(t) \quad (4)$$

$$v(t + \delta t) = v(t) + \frac{1}{2} \delta t [a(t) + a(t + \delta t)] \quad (5)$$

where $a(t)$ is the acceleration.

In the current work, we consider a droplet consisting of 7,000 argon atoms, which corresponds to a diameter of approximately 5 nm. Argon is a simple monatomic, non-polar fluid without quantum effects, which has been shown to be represented with sufficient accuracy by the LJ potential. The atomic mass of argon, m , is 39.95 amu and its LJ parameters are $\sigma = 3.405 \text{ \AA}$ and $\epsilon/k_b = 119.8 \text{ K}$, where k_b is the Boltzmann's constant. All variables in the simulation can be expressed in reduced dimensionless form using the standard scales for a LJ fluid: σ as length scale, ϵ as energy scale and $\sigma\sqrt{m/\epsilon}$ as time scale, τ^* . The liquid substrate also consists of argon atoms and has dimensions of $(50, 20, 50)\sigma$, which corresponds to 205,000 atoms.

We use the LAMMPS computer code [11] to simulate the impacts of the liquid nanodroplets on a liquid layer. The simulation domain is a rectangular box of dimensions $(50, 100, 50)\sigma$ and periodic boundary conditions applied in all the three dimensions. A 3-dimensional spatial decomposition was used to parallelise the computation and the integration step, δt , was set to $0.009\tau^*$, which is approximately 0.02 ps. In the interest of computational efficiency, various values of the cutoff radius, r_c , were tested; results presented here correspond to the smallest radius used, 2.0σ .

The initial configuration of the system is shown in Figure 1. The droplet is initially placed in the void space above the liquid substrate at a large separation, i.e. many times the potential cutoff radius, to ensure no immediate interactions. The molecules of the droplet and liquid substrate were both initialised along an FCC lattice with a reduced density, ρ^* , of 0.75. The initial velocity of the atoms was taken from a Gaussian distribution such that the initial overall system reduced temperature, T^* , was 1.0.

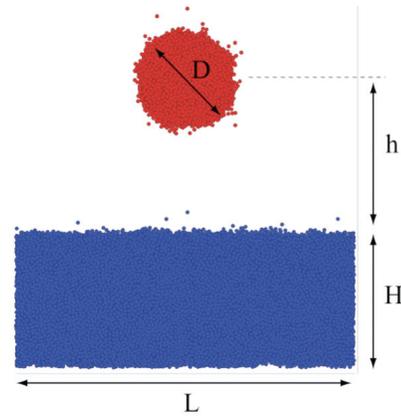


Figure 1: Initial system configuration with the important geometric parameters indicated.

From this initial configuration, the system was allowed to equilibrate for $2250\tau^*$ until its thermodynamic properties reached steady state (cf. Figure 2). After the equilibration phase, the system temperature settled to $T^* \approx 0.58$, which is approximately 69.5 K. Note that during this process a number of atoms evaporated from both the droplet and liquid substrate to create a uniform vapour environment filling the volume around the droplet.

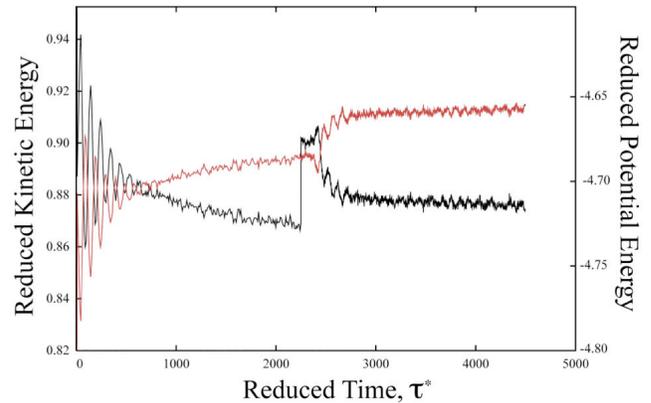


Figure 2: Reduced kinetic (black) and potential energy (red) of equilibration, impulsive acceleration and impact phases at $|v^*| = 0.228$.

Once the equilibration phase had been completed, an impulsive acceleration was applied to the droplet to start its motion towards the liquid substrate. This was achieved by adding a uniform velocity to the existing random molecular motion of those atoms that were still part of the droplet. More specifically, three velocities were used in the current study: 0.114, 0.228 and 0.307 in reduced units, which correspond to 18, 36 and 50 m/s, respectively. With the applied velocity the droplet was allowed to impact normally onto the liquid substrate and the resulting interactions were observed for another $2250\tau^*$ of runtime. This phase causes a significant increase in the kinetic energy as shown in

Figure 2. After the impact, the overall system temperature equilibrated at $T^* \approx 0.59$ for the slow droplet velocity, which is approximately 70.7 K. In all phases of the process, subcritical conditions were preserved.

3 RESULTS

In this section we present the most significant results of this study. Although the simulations were performed for all three velocities reported above, due to space considerations we are only presenting the results of the impacts at 36 and 50 m/s; these will be referred as slow and fast impact, respectively.

Initially, as the leading edge of the droplet approaches the liquid layer, it starts to interact with the atoms at the surface of the liquid substrate. When the approaching droplet enters within the cutoff distance of the potential, noticeable distortion and bridging is observed between the droplet and the liquid surface. This behaviour is shown in Figure 3 for a slice of $\pm 1\sigma$ about the median plane of simulation for the slow and the fast impact. In all figures, the atoms shown in red are those initially part of the droplet while those in blue were initially in the liquid layer. Comparing the relative degree of bridging that occurred between the three velocities studied the effect was seen to decrease with the increase of the impact velocity. This could be attributed to the fact that as velocity increases, the atoms at the leading surface of the droplet spend less time in the region of attraction where they can interact with the liquid surface prior to impact.

In Figures 4 and 5 we present different snapshots of the impact effects for a slice of $\pm 5\sigma$ about the median plane of the simulation domain in the slow and fast cases.

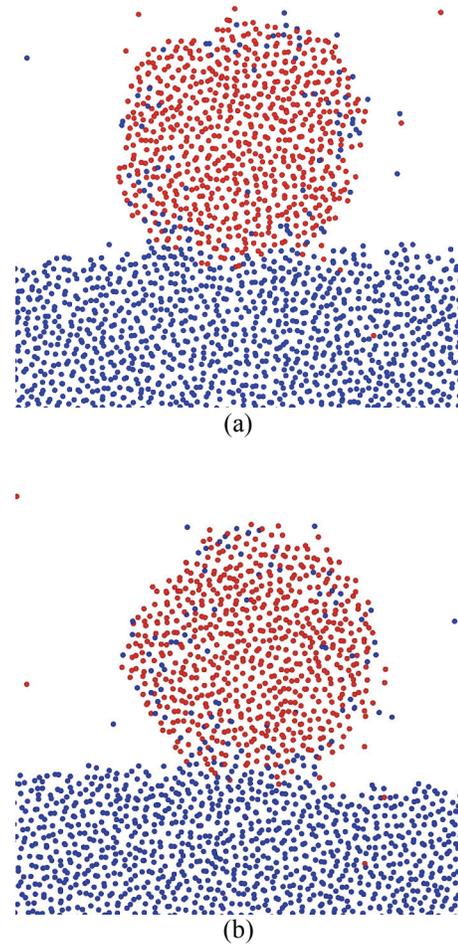


Figure 3: Interface bridging prior to impact: (a). $|v^*|=0.228$, (b). $|v^*|=0.307$.

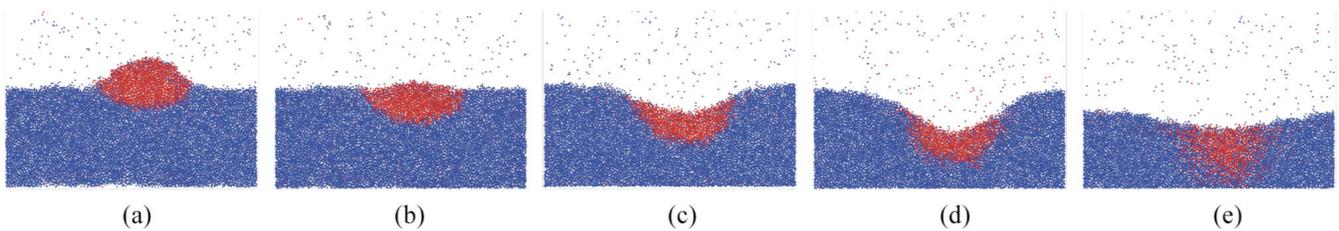


Figure 4: Impact effects at $|v^*| = 0.228$.

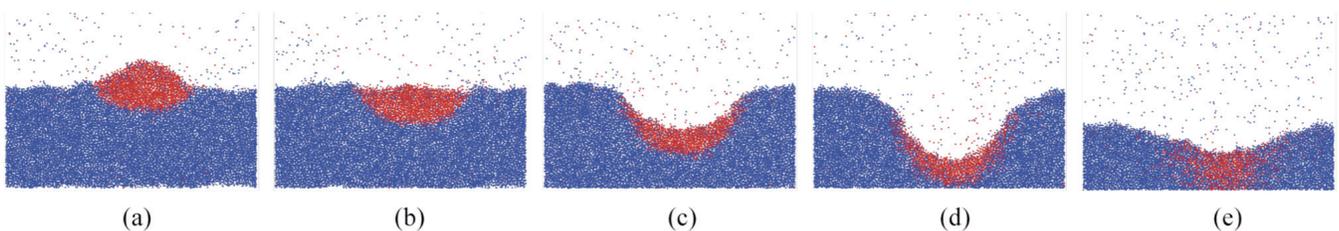


Figure 5: Impact effects at $|v^*| = 0.307$.

When the droplet centre of mass begins to approach the level of the undisturbed surface, the liquid substrate begins to be displaced by the droplet and a crater begins to form. As the crater grows, the droplet spreads along the bottom and walls of the crater. As the velocity of the impacting droplet increases, both the speed and depth of the crater formed increase. Despite the significant crater at all velocities, no rapidly forming corona was observed around the initial area of impact.

Once the impact energy of the droplet has been fully dissipated by the deformation of the liquid substrate, the crater begins to collapse and the surface of the liquid substrate begins to smooth. At the same time, due to the intimate contact between the droplet and the liquid of the substrate, the atoms of the droplet start to diffuse into the bulk liquid. In all three impact velocities studied, the nanodroplet was observed to coalesce and eventually get absorbed into the liquid substrate. For coalescence to occur, the vapour layer between the liquid substrate surface and the droplet must be ruptured [1]. Here the rupture is promoted by the low argon vapour density and the relatively high droplet velocity. In all cases, the phenomena are more pronounced with the increase of velocity.

4 CONCLUSIONS

In this paper, we have presented a molecular dynamics approach to model the dynamic behaviour of liquid nanodroplets impacting on liquid substrates. We considered liquid droplets of 5 nm in diameter, consisting of 7,000 atoms interacting via the Lennard-Jones potential. We simulated the impulsively accelerated movement of such droplets and their splashing on a liquid layer of 205,000 atoms. The impacts at three velocities are characterised by a series of similar events of increasing effect with velocity. As the droplet approached the surface noticeable bridging was observed. The impact created a deep crater leading to coalescence and droplet absorption before the layer's smoothing.

The coalescence and absorption under these conditions is an important finding for many applications where the target is the accelerated delivery of nanodroplets into liquid layers, like drug delivery, coating, and fabrication applications.

The particular physical mechanisms revealed, show the significance of the atomistic treatment of phenomena at this length scale, as this type of behaviour is very difficult to be modelled with continuum mechanics approaches.

We are currently extending our study to increase the size of the system. Besides being more realistic, the larger substrate will account for the minimisation of possible boundary effects (waves at the edges). In addition, by increasing the depth we will be able to explore further if the formation and propagation of a vortex sheet into the surrounding quiescent fluid occurs in the coalescence phase of this process. In this case, we have increased also the time length of our simulations to account for possible recoiling

of the crater and determine if jetting effects could be produced.

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