A Continuum and Molecular Dynamics Simulation of Nano-droplets Collision

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Abstract

The extent to which the continuum treatment holds in binary droplet collisions is examined in the present work by using a continuum-based implicit surface capturing strategy (Volume-of-Fluid coupled to Navier-Stokes) and a molecular dynamics methodology. The droplet pairs are arranged in a head-on-collision configuration with an initial separation distance of 5.3 nm and a velocity of 3 ms\(^{-1}\). The size of droplets ranges from 10 to 50 nm. Inspecting the results, the collision process can be described as consisting of two periods: a pre-impact phase that ends with the initial contact of both droplets, and a post-impact phase characterized by the merging, deformation, and coalescence of the droplets. The largest difference between the continuum and MD predictions is observed in the pre-impact period, where the continuum-based viscous and pressure drag forces significantly overestimate the MD predictions. Due to large value of Knudsen number in the gas (\(Kn_{\text{gas}} = 1.972\)), this behavior is expected. During the post-impact period, both MD and continuum-based simulations are strikingly similar, with only a moderate difference in the peak kinetic energy recorded during the collision process. With values for the Knudsen number in the liquid (\(Kn_{\text{liquid}} = 0.01\) for \(D = 36\) nm) much closer to the continuum regime, this behavior is expected. The 50 nm droplet case is sufficiently large to be predicted reasonably well with the continuum treatment. However, for droplets smaller than approximately 36 nm, the departure from continuum behavior becomes noticeably pronounced, and becomes drastically different for the 10 nm droplets.

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INTRODUCTION

Over the last decade or so, significant engineering interest has been focused on time and length scales where the continuum approximations become questionable. For multiphase flow applications, in particular the gas-liquid system, the situation can be problematic since the large discrepancy in the respective mass densities of each phase can give rise to situations where the continuum treatment (i.e. application of continuum level equations) may hold reasonably well in the liquid phase, but not so well in the gas phase. This line of thought is in agreement with Sharp et al. [1], where it is argued that liquids continue to follow the continuum regime for length scales that are about two orders smaller than gaseous flows.

Out of the large variety of configurations in gas-liquid system, a recurring and common configuration consists of colliding liquid droplets. The continuum-level binary droplet collision phenomenon has been previously investigated in detail [2-6]. But the literature is very limited for droplets having nanometer scale dimensions. The first systematic investigation for nanoscale binary droplet collision was done by Ming et al. [7], where they concluded that continuum-level droplet collision models are applicable for nanometer scale Argon clusters. Subsequent MD simulations of Argon nano-droplet collisions [8-9], report a classification of the collision process while a study by Kim [10] on polymer droplets was aimed at characterizing the deformation process and the contact radius evolution, in comparison to the continuum Hertzian model of solid elastic balls.

While some knowledge of the nano-droplet collision process has been developed, the focus of these works was not directed at understanding and characterizing the departures from continuum behavior that occur with decreasing droplet size. In the present work, this topic is taken by combining MD [11, 12] and continuum level simulations [13] of binary droplet collisions, and by exploring the discrepancies in collision behavior. The systems studied consist of Argon droplets undergoing binary head-on collisions with diameters ranging from 10 nm to 50 nm. The main reason for choosing Argon is that its interatomic potential has a relatively simple form and is adequately represented with Lennard-Jones potential. Furthermore, the reported MD simulations employed one million atoms and are able to simulate the entire droplet collision process within reasonable time. This provides attractive conditions from which to compare to continuum level simulations.

NUMERICAL METHODS: Volume of Fluid

The code used in the present work pertains to an open source solver (interFoam), which forms part of a larger distribution of computational mechanics solvers and C++ libraries of OpenFOAM®.

In the present case, an incompressible treatment is enforced, i.e. \( \nabla \cdot \mathbf{u} = 0 \). The first part of the solution consists of the transport of the local liquid fraction, \( \alpha \), which is defined at the computational cell level (\( \Omega_i \)), i.e.

\[
\alpha(x,t) = \frac{1}{|\Omega_i|} \int_{\Omega_i} \mathbb{I}(\chi, t) dV,
\]

where \( \mathbb{I} \) is a liquid phase indicator function and is defined as one at points occupied by liquid and zero at points where gas is present. The discrete finite volume solution for the transport of \( \alpha_i \) (corresponding to cell i) is obtained from

\[
\frac{\alpha_i^{n+1} - \alpha_i^n}{\Delta t} = -\frac{1}{|\Omega_i|} \sum_{f \in \partial \Omega_i} (F_u + \lambda_M F_c)^n,
\]

where the unsteady term is discretized using forward Euler scheme, and the advection term appears as a summation over the cell faces (f) of \( \Omega_i \). Quantities evaluated at the faces are subscripted by f. The advection fluxes \( F_u \) and \( F_c \) are expressed by

\[
F_u = \phi_f \alpha_{f,u} \text{upwind},
\]

\[
F_c = \phi_f \alpha_f + \phi_{f,\alpha} (1 - \alpha)_f - F_u,
\]

where \( \phi_f \) (volume flux) is given by

\[
\phi_f = u_f \cdot S_f.
\]

The role of the delimiter \( \lambda_M \) in Eq. (2) is to separate the numerical treatment given to the evolution of the liquid fraction in the interfacial region as opposed to the single-phase region. Specifically, away from interface or its neighboring cells \( \lambda_M = 0 \) while at the interface \( \lambda_M = 1 \).

With respect to momentum, the following equation is solved

\[
\frac{\partial \rho \mathbf{u}}{\partial t} + \nabla \cdot (\rho \mathbf{u} \otimes \mathbf{u}) = -\nabla p_d + [\nabla \cdot (\mu \nabla \mathbf{u}) + \nabla \mathbf{u} \cdot \nabla \mu] - g \times \mathbf{x} + \gamma_{\nabla \cdot \alpha} \nabla \cdot \alpha
\]

where the Continuum Surface Tension model of [14] is employed to treat the surface tension force. As is usually done in implicit interface capturing strategies, the density and viscosity fields are computed by

\[
\rho = \rho_1 \alpha + \rho_g (1 - \alpha),
\]

\[
\mu = \mu_1 \alpha + \mu_g (1 - \alpha).
\]
NUMERICAL METHODS: Molecular Dynamics

A truncated and shifted Lennard-Jones (LJ) 12-6 pair potential is employed in the present work, namely

\[ V_W = 4\sigma^6 \left[ \left( \frac{\sigma}{r_{cut}} \right)^{12} - \left( \frac{\sigma}{r_{cut}} \right)^6 \right] - 4\epsilon \left[ \left( \frac{\sigma}{r_{cut}} \right)^{12} - \left( \frac{\sigma}{r_{cut}} \right)^6 \right] r < r_{cut}, \]

\[ 0 \quad r \geq r_{cut}, \]

with parameters \( \sigma = 0.341 \text{ nm} \) and \( \epsilon = 10.3 \text{ meV} \), to describe interatomic forces for Ar - Ar interactions [15]. The cutoff distance is \( r_{cut} = 2.5\sigma \). The long-range corrections of the pressure and potential energy are not considered, as they cannot be applied consistently when multiple phases with widely different densities coexist in the same simulation cell. The velocity Verlet algorithm with a time step size of 0.006 picoseconds (ps) is used to integrate the equations of motion in all MD simulations [16].

To provide fluid property data to continuum level simulations, equilibrium MD (EMD) simulations are first performed to determine the saturation pressure, surface tension [17-18], density and viscosity [19] of saturated liquid and vapor of Ar at a temperature of 85 K, which is about 7% higher than the melting temperature of solid Ar. These fluid properties are used as inputs to the VoF equations and are tabulated in Table 1.

### Table 1. Fluid properties of Ar at 85 K determined from EMD simulations.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( P_{sat} ) (Pa)</td>
<td>2.17 x 10^8</td>
</tr>
<tr>
<td>( \gamma_{lv} ) (mN/m)</td>
<td>8.16 ± 0.04 x 10^-3</td>
</tr>
<tr>
<td>( \rho ) (kg/m^3)</td>
<td>1310</td>
</tr>
<tr>
<td>( \mu ) (mPa*s)</td>
<td>190 ± 1 x 10^-6</td>
</tr>
<tr>
<td>( \rho_v ) (kg/m^3)</td>
<td>13</td>
</tr>
<tr>
<td>( \mu_v ) (mPa*s)</td>
<td>7.0 ± 0.1 x 10^-6</td>
</tr>
</tbody>
</table>

**Continuum Model**

The properties for both liquid and vapor phase are obtained from Table 1 computed in the previous section. The velocity field at all points within the droplets is initially assigned a velocity magnitude of \( V_o \) (i.e., relative velocity between them is \( 2V_o \)). The system parameters employed in both MD and VoF simulations are listed in Table 2 in both dimensional and non-dimensional form along with the key non-dimensional numbers.

### Table 2. Benchmark parameters employed in the MD and continuum VoF simulations in dimensional and (non-dimensional) form.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values (Non-dimensionalized)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interdroplet spacing - ( L_g )</td>
<td>5.3 nm (0.1472)</td>
</tr>
<tr>
<td>Diameter of Droplet - ( D )</td>
<td>36 nm (1)</td>
</tr>
<tr>
<td>Initial Droplet Velocity - ( V_o )</td>
<td>3ms^-1 (1)</td>
</tr>
<tr>
<td>Liquid Reynolds Number - ( Re_L )</td>
<td>0.745</td>
</tr>
<tr>
<td>Liquid Weber Number - ( We_L )</td>
<td>0.052</td>
</tr>
</tbody>
</table>

**Collison Simulation Setup**

This section presents the parameters and setup employed in both methodologies for the benchmark case of droplets having \( D = 36 \text{ nm} \). The system under consideration is initialized with two identical argon droplets in a saturated argon environment with a given initial velocity of \( V_o \) (i.e., relative velocity between them is \( 2V_o \)). The domain length, grid size and time step size used for the benchmark case are 100 nm, 1 nm and 1 ps respectively.
The MD Model

Using the Berendsen thermostat \([20]\), the system of a 100-orientated perfect FCC crystal Ar (see Figure 2(a)) is equilibrated at a temperature of 85 K, which is naturally the same temperature at which the EMD calculations were performed. The original crystal Ar soon melted and partially vaporized to establish a liquid-vapor coexisting phase in the simulation box. To distinguish the liquid and vapor phases in the simulation, an Ar atom is defined as liquid if its potential energy is lower than half of that in a saturated bulk liquid at 85 K. This half value cut-off for phase determination is arbitrary but faithfully reflects the physical transition occurring in the interfacial region. Additionally, the method of distinguishing the phase based on potential energy has a lower computational cost than the density criterion and avoids the undesirable dependency on the size of the subdomain needed for density calculation. It has also been successfully used in study of coalescence of nanoscale droplets on a solid surface \([21]\). After 2,000 ps, the system reaches a steady state and a spherical-shaped liquid Ar droplet is formed in the center of the simulation box. To study the collision of two droplets using MD simulations, the liquid-vapor coexisting phase in the simulation box is duplicated in the x direction to create two identical liquid Ar droplets. The new system contains 1,000,000 Ar atoms and the separation between the two Ar droplets is \(L_g\) (see Fig. 2(c)). To make the two droplets collide, an x-direction velocity of \(\pm 3\) ms\(^{-1}\) is assigned to liquid atoms in the left/right half of the simulation box respectively and constant-NVE simulations are carried out for a time period of 6,000 ps.

COMPARISON METRIC

To aid in the selection of a suitable metric for describing the collision process, results from a continuum simulation are depicted in Fig. 3 in terms of liquid bulk kinetic and surface energy. The surface energy trend displays a monotonic decrease from the two droplet configuration to a single droplet coalescence.

However, the kinetic energy, defined as,

\[
KE_{VOF} = \int_{\Omega_{\alpha \geq \text{threshold}}} \frac{1}{2} \rho u^2 d\mathbf{v},
\]

shows a much more interesting trend characterizing the different stages during the collision process. Here \(\Omega\) represents the entire domain and the integration is computed over the cells where liquid phase volume fraction is greater than or equal to a threshold value.

For the cases pertinent to this problem, a threshold value of 0.1 provides adequate answers, i.e. having a lower positive threshold leads to very similar values, since the gas phase density is so much lower than the liquid one.

Due to the more descriptive characterization of collision afforded by the kinetic energy, it is used as a metric of comparison between MD and continuum simulations in the calculations presented in this paper.

In MD, the cylindrical symmetry of the problem is exploited to compute liquid kinetic energy as shown in Fig. 4. The intent is to capture the macroscopic local fluid velocity in the droplets and not the microscopic the-

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**Figure 2.** Schematic diagram of the procedure for generation of two droplets: (a) a cubic Ar crystal in the center of a big simulation box; (b) a liquid Ar droplet surrounded by its saturated vapor; and (c) two identical droplets created by duplication of the simulation box in the x-direction.

**Figure 3.** Continuum simulation log-linear plot for kinetic energy and surface energy for a case of droplet diameter \(D = 36\) nm and \(\Delta t = 1\) ps.
Figure 4. The schematic diagram of a typical bin used for velocity and kinetic energy calculations. The projection of the bin in the y-z plane has a ring shape with the difference between inner radius and outer radius of 2 nm. The thickness of the bin in the x-direction is 2 nm. $(y_c = 28.3 \text{ nm}, z_c = 28.3 \text{ nm})$ indicates the center of the ring. $y_i$ and $z_i$ are, respectively, y and z coordinate of atom i. $\theta$ is the azimuth angle of atom i.

Normal velocity. It is determined by averaging velocities of atoms in bins with the width of 2 nm along the axis of cylinder (the axis connecting the center of mass of two droplets) and 2 nm along the radius of cylinder. In each bin the axial velocity, $V_x$, and radial velocity, $V_r$, are determined by,

\[
V_x = \frac{1}{N} \sum_{i=1}^{N} v_{x,i} \\
V_r = \frac{1}{N} \sum_{i=1}^{N} \left( v_{y,i} \cos \theta + v_{z,i} \sin \theta \right),
\]

where $v_{x,i}, v_{y,i}, v_{z,i}$ are respectively the x, y and z component of velocity of atom i in the bin, N is the number of atoms in the bin, the summations are over all liquid atoms in the bin, and $\theta$ is the azimuth angle as shown in Fig. 4. Accordingly, the kinetic energy of liquid in each bin is given by

\[
KE_{MD}(x,r) = \frac{1}{2} \rho_n \pi \left( r + \frac{\Delta r}{2} \right)^2 \Delta r \Delta (V_x^2 + V_r^2).
\]

The total kinetic energy of the liquid phase is the summation of $KE_{MD}(x,r)$ in all bins.

**NANO-SCALE DROPLET COLLISION**

In the first part of this section, we take a detailed view of the comparison between MD and continuum droplet collision calculations presented in Figure 5. This is followed by a comparison of collisions for pairs of droplets having different sizes, where the point of interest is the degree of departure from continuum behavior.

**Similarities and differences between MD and Continuum level predictions**

By considering the time histories of kinetic energy for both MD and continuum shown in Fig. 5 ($D = 36$ nm), it is natural to consider two periods in the collision process.

The first period corresponds to the pre-impact phase and it is marked by the deceleration of droplets due to the increase of pressure between them and the action of viscous drag forces. The second period is characterized by the coalescence of the droplets.

The differences between the MD and continuum results extend beyond the VoF numerical resolution of the velocity field. To gain a better appreciation of the difference, we consider the Knudsen number (Kn), as categorized by el Hak [22], namely

1. $Kn \leq 0.001$ (Continuum),
2. $0.001 < Kn \leq 0.1$ (Slip-flow),
3. $0.1 < Kn \leq 10$ (Transition (moderately rarefied), and
4. $Kn > 10$ (Free molecular flow)

In our particular case, for the gas phase we have from [22]

\[
\lambda = \frac{k_B T}{\sqrt{2 \pi P \sigma^2}} = 10.45 \text{ nm}, \quad (14a)
\]

\[
Kn_{gas} = \frac{\lambda}{L_g} = 1.972. \quad (14b)
\]

where $k_B$ is Boltzmann constant, $P_{sat}$ value is used for the value of pressure (P) and $\sigma$ value is taken from table IV. For liquid phase, using an estimate of lattice spacing as a substitute for mean free path [1] the following values are obtained

\[
\delta \sim \left( \frac{V}{N_A} \right)^{1/3} = 0.36 \text{ nm}, \quad (15a)
\]
\[ Kn_{\text{liquid}} = \frac{\delta}{D} = 0.01. \]  

(15b)

The value of \( \bar{V} \) is taken from Table 4 and \( N_A \) represents Avogadro’s number. The corresponding Kn value puts the gaseous flow for this system in a moderately rarefied flow regime, while the liquid is in the slip flow regime. While neither phase is expected to behave as a continuum, the deviation from continuum behavior is milder for the liquid phase due to its much lower value of Kn.

Consistent with this Kn characterization, the discrepancies observed in the pre-impact period are not only caused by velocity field representation in VoF simulations as previously discussed, but also by the departure from continuum behavior. The interdroplet spacing, \( L_g \), is simply too small to expect the Navier-Stokes to hold in this region. Similar observations have been presented in the literature (e.g. the work of Sirk [23]).

While viscous forces may contribute to the deviation occurring between MD and continuum calculations, the stress tensor (T) solved in the Navier-Stokes also contains a pressure component (i.e. \( T = -PL + \mu_g (\bar{V}u + \bar{V}u^T) \)). To see its effect in the collision process, the viscosity (\( \mu_g \)) is set to zero and the calculation for the kinetic energy is repeated. The results, presented in Fig. 6, show a less pronounced reduction in kinetic energy when compared to the finite viscosity case. However, at earlier times during the pre-impact phase the results are similar between both viscosity cases. Also, during this period both continuum calculations predict a kinetic energy that is substantially lower and decays in a qualitatively different manner compared to the MD results. This decay in kinetic energy is attributable to the stagnation pressure build-up in the interdroplet spacing region, which is specific to the continuum treatment. This trend is not observed in MD calculations. In fact in MD, the kinetic energy decay is almost linear; it does not have the exponential decay observed in VoF simulations.

From Figure 6, the post-collision stage begins at approximately 500 ps. Although the peak in kinetic energy is somewhat higher for the MD predictions, the trend in the kinetic energy rise and fall is strikingly similar between both solution methods. This behavior essentially means that once the droplets have coalesced and the dynamics are governed by the liquid phase, the notable differences between MD and continuum behavior diminished considerably. Again, making note of the respective Kn values, the corresponding liquid phase quantity is much closer to the continuum regime, and thus, this approximation to Navier-Stokes behavior is to some degree expected. The difference in peak kinetic energy between MD and VoF is, at least, partially attributable to the constrained no-slip flow during this period (Kn_{liquid}=0.01).

**Size effect on droplet collision**

Prediction of kinetic energy time histories for both MD and continuum level simulations are shown in Figure 7 corresponding to droplets having a size of \( D = 10 \)
nm, 20 nm, 28 nm, 36 nm, and 50 nm. In all of these calculations, the initial velocity of the droplets and interdroplet spacing remain the same as indicated in Table 2. The time step and grid size used in VoF are respectively 1 ps and 1 nm.

Overall, the trend is one of increasing similarity between the two different sets of results as the droplet size increases. The most noticeable difference is the pre-impact behavior. The Knudsen value for the gas remains the same (same interdroplet spacing) as the benchmark case, and is thus within the moderately rarefied regime. With decreasing droplet size, the discrepancy between MD and continuum predictions become much more pronounced, as the time required for impact increases from $t_{impact} \approx 0.8$ ns for D =50 nm to no impact observed for D =10 nm. The reason behind this trend is explained by considering the ratio of droplet inertia to resistance forces, e.g. viscous and pressure build up. This is equivalent to the Reynolds number, which shrinks with decreasing D. Hence, for a critical value of the Reynolds number, the resistance forces will be such that they will completely impede droplet contact.

With respect to the liquid phase dynamics, the Knudsen remains within the slip flow regime. Provided the droplets are sufficiently large to produce impact, the results show that the relative magnitude for the peak in kinetic energy, between MD and continuum simulations, increases with decreasing droplet size. However, it is the pre-impact period that exhibits the strongest departure from continuum behavior.

CONCLUSIONS

The current work presents a direct comparison between molecular dynamics and continuum level (Navier-Stokes with Volume-of-Fluid) simulations of binary droplet collision for nanometer sized Argon droplets. The results show that both methodologies predict reasonably similar behavior as the droplet diameter approaches 50 nm. At the other extreme, for droplets having diameters at or below 10 nm, the trends, characterized by kinetic energy time histories, show markedly different behavior. A prominent aspect of the MD/continuum difference occurs during the trajectory of the droplets through the gas phase before any contact has been established. During this pre-impact period, continuum simulations largely over-predict the degree of resistance, contributed by both viscous and pressure effects, resulting in a strong decline in the kinetic energy, and consequently a longer time for contact to occur. In fact, for sufficiently small droplets (D < 28 nm), this impact never occurs. Due to the large value for the Knudsen number corresponding to droplet-gas interactions ($Kn_{gas} \approx 1.972$), this behavior is expected. Conversely, once the droplets have made contact, the surface tension forces immediately act to produce coalescence with little to no secondary oscillations. This post-impact period sees good agreement between MD and continuum simulations. The liquid based Knudsen number ranges between 0.036 and 0.0072 for respective droplet diameters between 10 nm and 50 nm, and thus the dynamics are expected to be much closer to the continuum behavior than the corresponding pre-impact period.

The conclusions from this work can be extended to systems of nano-droplets. If the droplets are smaller than 50 nm, it is expected that some degree of departure from continuum based behavior will result for the prediction of movement of these droplets within the gas phase. In fact, it is this motion where the deviations from continuum behavior are the strongest. Thus, for a cloud of nano-droplets where their size is significantly below the 50 nm mark, it is envisioned that the droplet transport will significantly depart from continuum behavior. Once collisions have occurred, however, the similarities with continuum behavior are strong.

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