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<td><strong>Date</strong></td>
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<td><a href="http://hdl.handle.net/10220/45836">http://hdl.handle.net/10220/45836</a></td>
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NUMERICAL STUDY OF SURFACTANTS’ EFFECT IN SURFACE AGGLOMERATION DURING 3D NANO-INKJET PRINTING BY MANY-BODY DISSIPATIVE PARTICLE DYNAMICS

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ABSTRACT: Surfactants are necessary in very small scale 3D inkjet printing in order to control and reduce agglomeration leading to nozzle clogging. This numerical study specially focuses on nano-droplet formation that takes place at the nozzle. As nano-droplet formation can be modelled by Many-Body Dissipative Particle Dynamics (MDPD), this methodology is employed for the implementation surfactants to study its performance on reducing agglomeration and effects on nano-droplet formation. The surfactant is implemented in MDPD as a simple molecule composing of single hydrophilic bead and single hydrophobic bead. Additional attraction parameters to properly implement the surfactants are a major feature of this study. Present findings indicate that a sufficient small amount of surfactant can effectively reduce ink deposition on the nozzle wall, in line with actual commercial references. From this work, we can conclude that the MDPD is an appropriate meso-scale simulation technique to numerically study nano-scale 3D inkjet flow dynamics, and to predict associated trends.

KEYWORDS: Many-Body Dissipative Particle Dynamics (MDPD), 3D inkjet printing, surfactant, ink deposition, agglomeration.
INTRODUCTION:

Nano-droplet formation is one of the most interesting phenomena to be studied in order to progress nano-scale 3D inkjet printing. As experimental observation of nano-droplet formation is technically challenging and expensive, numerical studies can provide a low-cost but accurate alternative. Out of the various numerical methods available, meso-scale simulation by coarse graining of standard empirical molecular dynamics simulation is found to be most effective for the investigation of this nano-droplet formation phenomenon, which has a length scale in the range of 100-1000nm (Fermeglia et al. (2009)). The printing fluid most commonly used in 3D inkjet printing technologies is polymeric ultraviolet ink, and the dissipative particle dynamics (DPD) method, a particle-based meso-scale simulation technique first introduced by Hoogerbrugge and Koelman (Hoogerbrugge et al. (1992)), is a suitable simulation technique to capture polymeric behavior and agglomeration in the ink with high accuracy (Aphinyan et al. (2017)). However, DPD with only pure repulsive force representation requires an extended version, the many-body dissipative particle dynamics (MDPD) method, to simulate the nano-droplet formation phenomenon. The MDPD was first initiated by Pagonabarraga and Frenkel in 2001 (Pagonabarraga et al. (2001)) to study free surface and vapor-liquid coexistence problem (Warren (2003), Ghoufi et al. (2012), Ghoufi et al. (2013), Atashfrooz et al. (2016), Yong (2016), Yong et al. (2016)). With inclusion of attractive force in MDPD, gas-liquid interface can be represented and hence, nano-droplet formation of the UV ink becomes possible to model. Accordingly, MDPD is a promising methodology to numerically determine the conditions necessary for generating nano-droplet formation in 3D nano-scale drop-on-demand inkjet printing.

To achieve continuous nano-scale flow and good working conditions of the nozzle, a major challenge to be addressed and resolved is the issue of ink fluid agglomeration, especially at very small scales where there will be significantly higher likelihood of nozzle clogging (Ivanova et al. (2013)). From earlier published experimental data, it was found that clogging results from the competition between particle–fluid, particle–surface and particle–particle interactions (Henry et al. (2012)). Our earlier study (Aphinyan et al. (2017)) has investigated the agglomeration within the ink, which can be considered to arise from particle–fluid and particle–particle interactions. The present study will progress to examine additionally particle–surface interactions, mainly focusing on the interaction between ink and nozzle’s wall. This form of agglomeration can be viewed as a potential source for deposit accumulation on the inner surface of nozzle leading to nozzle clogging. The effectiveness of using surfactants to control and reduce such agglomeration is investigated in detail here. In this case, it is necessary to add a surfactant model to the MDPD simulation setup described in our previous study (Aphinyan et al. (2017)). The MDPD surfactant will be implemented by the explicit method, whereby the attraction parameters are calculated based on its molar volume and solubility parameter, similar to the calculation of repulsion parameters in DPD simulation of UV inks commonly used in 3D inkjet printing nowadays. The computation is described in detail in the next section.

SIMULATION METHOD:

MDPD simulations were carried out via the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) MD software (Plimpton (1995)). The size of the simulation box was set as $60 \times 60 \times 300 \sigma_{L}$ with non-periodic boundary conditions, such that number density is equal to 6, following the standard density of following the standard density of MDPD beads (Warren (2003), Lin et al. (2006), Chen et al. (2010)). The model composed of two main parts: the nozzle and polymeric ink. The nozzle has a cylindrical body and conical tip as shown in Figure 1. The
cylindrical body has an inner and outer radius of $7r_e$ and $10r_e$ respectively. The cone of the nozzle has a slope of $30^\circ$ and the radius of the orifice, or the nozzle’s tip, is $r_e$. The coarse-grained models are generated by directly coarse-graining from the atomistic model. The main constituents of polymeric UV ink in this study are the oligomers, monomers and surfactants. One of the main quantitative outcome of this study is to determine the optimal amount of surfactant in the ink compositions compared to actual amounts used in commercial applications. The ink contains 16,400 MDPD beads of oligomers, monomers and a photo-initiator, in the ratio of 2.5:1:0.4. An oligomer is made up of 6 connected beads of monomer, bonded together with a harmonic bond potential with bond force constant set to be 64. Surfactant is implemented in MDPD as a simple molecule composing of single hydrophilic bead (H) and single hydrophobic bead (T). To facilitate coarse graining, the simulation is performed in reduced unit.

![Figure 1: The geometry of the nozzle in this MDPD simulation.](image)

The scheme of MDPD inherits the three main forces of DPD, which are the conservative force, the dissipative force and the random force, as shown in Equation 1 below.

\[
F_{ij} = F_{ij}^C + F_{ij}^D + F_{ij}^R
\]

\[
F_{ij}^C = A_{ij} \omega^C(r_{ij}) e_{ij} + B_{ij}(\rho_i + \rho_j) \omega^d(r_{ij}) e_{ij}
\]

\[
F_{ij}^D = -\gamma \omega^d(\eta_{ij}) \eta_{ij} \cdot v_{ij} e_{ij}
\]

\[
F_{ij}^R = \sigma \omega^R(\eta_{ij}) \theta_{ij} e_{ij}
\]

$F_{ij}^C$ is a conservative force, $F_{ij}^D$ is the dissipative force as a fictional effect that reduces velocity deviation among particles and $F_{ij}^R$ is the stochastic force. These three components of forces can be written independently in terms of exerted force of particle $i$ on particle $j$ as shown in Equations 2 to 4. Here, $A_{ij}$ and $B_{ij}$ are the parameters of attractive force and repulsive force between particle $i$ and particle $j$ respectively, $\sigma$ is a thermostat-rely coefficient, $F_{ij}, \eta_{ij}, v_{ij}, \theta_{ij}, e_{ij}$ is the force, distance, velocity, a Gaussian random variable with zero mean and unit variance, and unit vector between particle $i$ and particle $j$ respectively.
In the conservative force of MDPD, the attractive force is defined as a linear function of $\eta_{ij}$ using the $\omega^c$ weight function, while the repulsive force includes a density-dependent term and the $\omega^d$ weight function. The weight functions and density terms are defined in Equation 5-7 below.

$$\omega^c(\eta_{ij}) = \begin{cases} 
1 - \frac{\eta_{ij}}{r_c}, & \eta_{ij} \leq r_c \\
0, & \eta_{ij} > r_c 
\end{cases} \quad (5)$$

$$\omega^d(\eta_{ij}) = \begin{cases} 
1 - \frac{\eta_{ij}}{r_d}, & \eta_{ij} \leq r_d \\
0, & \eta_{ij} > r_d 
\end{cases} \quad (6)$$

$$\rho_i = \frac{16}{\pi r_d^2} \sum_j (1 - \eta_{ij}/r_d) \quad (7)$$

$r_c$ and $r_d$ are the cut-off radius of the attractive force and repulsive force respectively and $\rho_i$ is the local density in discrete computing that is equal to the linear summation of finite beads. The weight functions $\omega^c(r)$ and $\omega^d(r)$ are valid in the conditions of $r < r_c$ and $r < r_d$ respectively.

For the terms of dissipative force and random force, $\omega^D$ and $\omega^R$ are weight functions which represent dissipative and stochastic position dependent weight functions respectively and the theorem of fluctuation-dissipation are given as

$$\omega^D(\eta_{ij}) = [\omega^R(\eta_{ij})]^2 = \begin{cases} 
(1 - \frac{\eta_{ij}}{r_c})^2, & \eta_{ij} \leq r_c \\
0, & \eta_{ij} > r_c 
\end{cases} \quad (8)$$

$$\sigma^2 = \frac{2\gamma k_B T}{m} \quad (9)$$

The thermostat used for MDPD is the same as thermostat of DPD. Equation 8-9 is the theorem of fluctuation-dissipation for the DPD simulation where $T$ is the equilibrium temperature of the system and $k_B$ is the Boltzman constant (Español et al. (1995)). These equations are similar to a isotropic Galilean invariant thermostat which can preserve hydrodynamics principle because they depend on relative velocities and the interactions among particles (Junghans et al. (2008)). All the basic MDPD simulation parameters, apart from $A_{sl}$, are summarized in Table 1.

**Table 1: A summary of MDPD simulation parameters.**

(Warren (2003), Lin et al. (2006), Chen et al. (2010), Yong (2016)).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>liquid density</td>
<td>$\rho$</td>
</tr>
<tr>
<td>repulsive force range</td>
<td>$r_d$</td>
</tr>
<tr>
<td>cut-off radius</td>
<td>$r_c$</td>
</tr>
<tr>
<td>liquid-liquid attraction</td>
<td>$A_{ll}$</td>
</tr>
<tr>
<td>liquid-liquid repulsion</td>
<td>$B_{ll}$</td>
</tr>
<tr>
<td>solid-liquid attraction</td>
<td>$A_{sl}$</td>
</tr>
<tr>
<td>solid-liquid repulsion</td>
<td>$B_{sl}$</td>
</tr>
<tr>
<td>coefficient for dissipative force</td>
<td>$\gamma$</td>
</tr>
<tr>
<td>coefficient for random force</td>
<td>$\sigma$</td>
</tr>
<tr>
<td>time step</td>
<td>$\Delta t$</td>
</tr>
</tbody>
</table>
Following the explicit method (Ghoufi et al. (2013)), in order to calculate the required attractive parameter between different liquid types, a specific UV ink commonly used in 3D inkjet printing nowadays are assumed (Aphinyan et al. (2017)). The ink compositions are of oligomers and monomers of polyethylene glycol (PEG) and polystyrene (PS) with benzophenone (BZP) as the photo-initiator. The surfactant used is sodium dodecyl sulfate (SDS). The attraction between each composition will be calculated based on its molar volume and solubility parameter (Ghoufi et al. (2013)). By calculating the Flory-Huggins ($\chi_{ij}$) parameters, the value of each pair of beads can be defined from the solubility parameter (Maiti et al. (2004)) in Equation 10,

$$\chi_{ij} = (\delta_i - \delta_j)^2 V_{ref}/kT$$  \hspace{1cm} (10)$$

where $\delta_i$ and $\delta_j$ are solubility parameters of an interacting pair beads, and $V_{ref}$ is the mean molar volume of each pair of beads. Then, the attraction parameter or interaction parameter, $a_{ij}$, also can be estimated as in Equation 11,

$$a_{ij} \approx a_{ii} + 0.606\chi_{ij}$$  \hspace{1cm} (11)$$

$a_{ii}$ is the attraction between the same kind of MDPD bead, and as discussed previously, this is set to -40. The attraction parameters within the whole ink system are illustrated in Table 2.

**Table 2: A summary of attraction parameters.**

<table>
<thead>
<tr>
<th></th>
<th>PEG</th>
<th>PS</th>
<th>BZP</th>
<th>SDST</th>
<th>SDSH</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG</td>
<td>-40</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS</td>
<td>-35.84</td>
<td>-40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BZP</td>
<td>-36.84</td>
<td>-39.56</td>
<td>-40</td>
<td></td>
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**RESULTS AND DISCUSSIONS**

Ink deposition on nozzle’s wall can be easily visualized in MDPD by looking at the amount of ink attached to the nozzle’s wall during the simulation. Pictorial representation of the MDPD simulation with different surfactant composition is provided in Figure 3. It can be observed that the main source for this type of agglomeration is clearly mostly due to monomer deposition. Figure 3 also shows that the loading amount of surfactant affects its performance, and that it can effectively reduce ink deposition as presented.
Figure 3: The ink deposition of PEG (red-monomer, oligomer), PS (blue-monomer, oligomer), surfactant (white-H, yellow-T) and photo-initiator (pink) by explicit method. The nozzle is hidden. (A) The UV ink without SDS. (B) The UV ink with 0.2% of SDS. (C) The UV ink with 0.6% of SDS. (D) The UV ink with 1.0% of SDS. (E) The UV ink with 3.0% of SDS. (F) The UV ink with 5.0% of SDS. (G) The UV ink with 7.0% of SDS and (H) The UV ink with 10.0% of SDS.

The quantitative result depicting the percentage of ink deposition on nozzle’s wall at different surfactant loading is presented in Figure 4. It can be seen clearly that increasing percentage by mass of surfactant reduces the deposition on the nozzle’s wall. The reduction is sharp when surfactant mass increases from 0 to about 1%, and it tapers off at surfactant mass above 1%. This phenomenon is similar to actual surfactants’ application, where only low amount of surfactant is sufficient to improve the ink’s hydrodynamic quality. From commercial references, the amount of surfactant inside UV ink compositions is normally less than 10 wt. % based on the total weight of the UV curable ink compositions (Van et al. (2011), De et al. (2016)). For more specific range in some available references of commercial UV curable inks, the amount of surfactants is usually used in the range between 0.2-3.0 wt. % (Ylitalo et al. (2003), Nakane et al. (2014), Saleh et al. (2017)). Thus, the simulation results of the implemented surfactant by MDPD is relatively close to the actual amount in commercial applications.

It is also apparent from Figure 4 that MDPD surfactant can effectively reduce ink deposition on the nozzle’s wall, reducing it by more than 60% at surfactant mass percentage of more than 1%.

![Ink Deposit on Nozzle's Wall](image)

Figure 4: Surfactant performance based on ink deposit on nozzle’s wall.

In addition, from Figure 4, we can also conclude that the surfactant, by itself, cannot effectively control the quantity of ink deposition. It is obvious that the ink deposition is still high, at 40%, even when a large amount of surfactant is applied. Thus, further de-agglomeration techniques must be considered for actual applications, in tandem with the addition of surfactant, to provide a sustainable printing conditions without nozzle clogging.

CONCLUSIONS

In this study, MDPD is used to effectively include surfactants in the simulation of the meso-scale process of nano-droplet formation. It was found that only small amount of surfactant (about 1%) is sufficient to reduce agglomerations on nozzle’s wall by up to 60%. Should there be a need to reduce ink deposition on nozzle’s wall further, this study showed that further addition of
surfactant cannot solve the problem. In this case, further de-agglomeration techniques must be considered. One such possibility is to chemically change the nozzle’s wall and ink interactions via the addition of a non-wetting coat.

REFERENCES


