Simulation & modelling of dilute solutions in drop-on-demand inkjet printing: a review

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ABSTRACT
This review is about the most important matters for advancing inkjet printing with a focus on piezoelectric droplet on demand (DOD) inkjet thin-film devices. The Nano material compounds can be incorporated into a polymeric matrix and deposited by piezoelectric inkjet printing. Current problems in advanced printers are discussed as embodied in liquid filament breakup along with satellite droplet formation and reduction in droplet sizes. Various model that predicts the printability of dilute, mono disperse polymer solutions in drop-on-demand “DOD” inkjet printing have been discussed. For satellite droplets, it is exhibited which liquid filament break-up treatment can be predicted via using a combination of two pi-numbers, including the Weber number. The layer was printed over other printed layers including electrodes composed of the conductive polymers and also several polymers. It has been discussed, some polymer materials are suitable for deposition and curing at low to moderate temperatures and atmospheric pressure, allowing for the use of polymers or paper as supportive substrates for the devices, and greatly facilitating the fabrication process. Furthermore, through this review, it has been discussed scaling analyses for designing and operating of inkjet heads. Because of droplet sizes from inkjet nozzles are typically on the order of nozzle dimensions, a numerical simulation is shown for explaining how to reduce droplet sizes through employing a novel input waveform impressed on the inkjet-head liquid inflow without changing the nozzle geometries. Regardless of their any less performance, inkjet printer head as a technique for the mentioned devices presents many advantages, the most notable of which are quickly fabricating and patterning, substrate flexibilities, avoidance of material wastage via applying “DoD” technologies.

Keywords: inkjet printing; drop-on-demand (DoD); carbon Nano tubes SWCNTs; ink polymers.

1. INTRODUCTION
1.1. Modeling of dod jetting.

Inkjet printing prepares digital pictures through producing and then transporting narrow ink droplets to printed surfaces. Recently, inkjet printing technologies have gone beyond just a computer printing process, and their prospects in several advanced technologies are very promising. Although various range of inkjet printing exists, two kinds have the most application for contemporary industrial applications, including continuous inkjet (CIJ) and drop-on-demand (DOD) [1-3]. Generally, for marking and coding of products and packages, a liquid inkjet is applied, that way forced to break up into droplets through pressure modulation [4, 5]. In CIJ system of inkjet printing, a strong pressure pump directs liquid ink from a reservoir and a microscopic nozzle, making a continuous stream of ink droplets based on the Plateau-Rayleigh instability [1, 2]. Through a piezoelectric, an acoustic wave creates and vibrates inside the print-head. Due to this vibration, the stream of liquids break into droplets at repetition rates around 65,000 to 150,000 droplets per second. The electrostatic field created by a charging electrode varies based on degree of drop deflection desired and results in the controlled electrostatic charge on each droplet [6-8]. Charged droplets via a few uncharged droplets which are known as guard droplets are separated for minimizing the electrostatic repulsion among adjacent droplets. The charged droplets are diverted through the electrostatic diversion plates to print on a receptor substrate. In any insufficient diversion, the droplets are collected to the further reusing. Usually, the small fractions of the droplets are applied for printing whereas the majorities are recycled. CIJs techniques with several major advantages are the oldest inkjet printing systems which have a high velocity of the ink droplets, allowing for a relatively long distance between print head and substrate, and a very high droplet ejection frequency. One of the major disadvantages of CIJ is a lower probability of nozzle obstruction due to the working of jetting system at all time. The major disadvantages of CIJ systems are the problem in sizes controlling, generating satellite, and splattering of the droplets on the target [9, 10]. In DOD, droplets are formed alternatively by the piezoelectric properties in response to discontinued pulses and pressures, respectively. In contrast to CIJ, no droplet deflection is applied for eliminating undesired droplets from depositing on a target. Therefore, DOD nozzle is located close to a target. For commercial systems, multiple nozzles are investigated for printing a few lines11-13]. Due to individual nozzle is fired independent of the other nozzles, with up to hundreds of nozzles in commercial equipment; each nozzle is inactive for wide duration of the time. For removing this matter, several mitigation plans are used, such as best formulations and intermittent purging [12, 13]. Commonly, no unique material of construction is required for DOD print head, usually making it cheaper and less complex to produce than CIJ system (Scheme 1). Scheme 1 exhibits the mechanisms of both DOD and CIJ systems. In CIJ, a continuous jet of ink released downward and progressively breaks into droplets where suitable droplets are directed to the paper and unsuitable ones are recycled.
to be used again. In DOD, ink droplets also travel downward but are separated uniformly because of their characteristics, such as route of stream and velocities, can be controlled via driving forces that might be either pressure or thermal activated [14,15].

The most commercial inkjet printers use the piezoelectric materials in an ink-filled chamber behind each nozzle instead of the heating elements. As soon as a voltage has appeared those materials generate the pressure pulses, consequently forcing a droplet of ink from the nozzle. Although Piezo inkjets allow a wider variety of inks to be used in comparison to thermal inkjets, Piezo print-heads are usually more expensive to manufacture because of the piezoelectric materials [10-14].

Using Piezo’s DOD, software controls the heads for applying a few droplets of ink per dot and these flexibilities are important when they are used in production lines for marking products. Requirements of this application are high speed, long service life and a relatively large gap between the print-head and the substrate (scheme 2). It exhibits the two details of Piezo DOD printing methods, and their droplet ejection mechanism. Inkjet printing technologies provide a process for producing individual or multiple droplets of liquid and then direct them toward the paper sheet via a digital controlling. Several materials and polymers with various functionalities can be coated through this system [10-14]. Generally, a digital fabrication inkjet printing presents the possibility for printing in macroscopic and even at a microscopic level and place the inks or materials where they are required, exactly. In addition, DOD coating method could be a possible way to paint materials. Therefore, the present study focuses on DOD technique due to its potential for broadening the applicability and high efficiency, particularly for painting. The theory of droplet formation of DOD on substrate is not yet fully understood due to the key stages during formation less than 100 µm. It is notable that the droplet diameter is around 40–50 µm and the details of such processes cannot be recorded by usually high-speed photography due to the 10,000 frame per second [12,15].

The moment equation can be written as \( \rho \frac{Du}{dt} = -\nabla P + \nabla \cdot \tau + \rho g \) (1) where, \( \rho \) is density, \( P \) is pressure, \( u \) is the flow velocity, “ \( t \)” is time and \( \tau \) is the stress tensor which is used in some inkjet printing for diluting the polymer solution in water. This equation can be rewritten in view of Cauchy stress tensor as: \( \sigma = \lambda (\nabla \cdot u) I + 2\mu e \) (2), where “I” is the identity tensor and \( \nabla \cdot u \) is the rate of expansion flow. In addition, the three dimensional trace of the stress tensor can be shown as: Trace (\( \sigma \)) = (3 \( \lambda + 2\mu \)) \( \mu \) (3) consequently, from the equations 2 & 3 the second viscosity can be defined as: \( \zeta = \frac{\lambda + 2\mu}{3\mu} \) (4) [16-18]. Both dynamic viscosity (\( \mu \)) and second viscosity (\( \zeta \)) must be constant; usually, both dynamic and second viscosities are related to the densities. Although the viscosities can be expressed via pressure, incompressible flows it would be interpreted by temperature. Since the divergence of \( \nabla u \) & (\( \nabla u \))T tensors are \( \nabla u \) & [\( \nabla (\nabla \cdot u) \)] (known as Lamb Vector) respectively, the most normal Navier–Stokes momentum equation can be written as: \( \rho \frac{Du}{dt} = -\nabla P + \mu \nabla^2 u + \frac{1}{3} \mu \nabla (\nabla \cdot u) + \rho g \) (5) [19-22]. Obviously, the volume viscosity “\( \zeta \)” is a mechanical pressure and is not equal to a thermodynamic pressure that is known as: \( \bar{P} \equiv P - \nabla u \) (6). The Stokes’ stress constitutive equation as \( \tau = 2\mu e \) can be written as: \( e = 1/2(\nabla u + (\nabla u)^T) \) that only used for incompressible viscous fluids as: \( \tau = \mu (\nabla u + (\nabla u)^T) \) (7). Due to \( \nabla u = 0 \) in an incompressible fluid, the momentum equation might be rewritten as: \( \frac{D\mu u}{dt} = (\mu \nabla u - \nabla^2 u = -\nabla \omega + g) \) (8) where \( \omega = \mu / \rho_0 \) is kinematic viscosity [23, 24]. There are five parts in the equation 8 including variation \( \frac{D\mu u}{dt} \), convection \( \nabla (\mu \nabla u) \), diffusion \( \nabla^2 \mu \), internal source \(-\nabla \omega \) and external source \( g \) respectively. The Laplacian “\( \nabla^2 u \)” is the difference between the velocity at a point and the mean velocity in a small surrounding volume and this parameter implies the diffusion of momentum [25].

1.2. Constitutive model.

FENE-CR [26], is a model for describing dilute polymer solutions in extensional flow and non-linear elastic dumbbell model can be written as: \( \sigma = 2\mu e + Gf(A - I) \) (9) where \( \mu_e \) is the solvent viscosity, \( E \) is the strain rate polymer stress tensor including elastic modulus \( G \), the conformation tensor \( A \) and “\( f \)” is the FENE factor which can be written as: \( f = \frac{l^2}{l^2 + 3(3/2\pi)(A)} \) where “\( l \)” is the accounts for the finite extensibility of the polymer’s chain. The extended equation is as: \( \frac{DA}{dt} = K.A + A.K^T - \frac{l}{T}(A - I) \) (10) where “\( \tau \)”, is the polymer’s relaxation time and \( K \) is the velocity. For a dilute polymer solution, the parameters in the FENE-CR model (elastic modulus \( G \), relaxation time \( \tau \) and finite extensibility \( L \), can be determined as functions of the molecular weight \( M_w \), weight fraction concentration \( \Theta \) and solvent quality factor \( \vartheta \) using Zimm theory [27]. The elastic modulus has a straight relationship to concentration and inversely relationship to...
molecular weight “$G = \frac{\partial T}{M_w}$” where R is the universal gas constant.

The dumbbell time relaxation “$\tau$” is defined as $\tau = \frac{1}{\lambda} \frac{[\mu]_t M_w}{RT}$ (11) where $\lambda \equiv \frac{\tau}{\tau} = \sum_i^{\infty} i^{3/2}$ is the universal ratio of the characteristic time relaxation ($\tau$) to the longest time relaxation ($\tau$). The intrinsic viscosity $[\mu]$ is explained via the Mark-Houwink formula as $[\mu] = KM_w^{3/2-\gamma}$ (12) where is a constant of polymer. $\lambda$ can be calculated from the ratio of the polymer folded to its fully extended length as: $L^2 = 3\left(\frac{\sin 3\gamma}{\cos M_{\mu}}\right) \left(C_{\cos M_{\mu}} \right)^{2(1-\gamma)}$ (13) where $\theta$ is the C-C bond angle and $j$ is the number of bonds in each monomer unit with molar mass $M_{\mu}$ and $C_{\cos}$ is the characteristic ratio[28]. For a dilute mono-dispersed polymer, the parameters of model in a solvent with quality factor, it can be shown $G = M_w^{3\gamma-2}$, $\tau = M_w^{3\gamma}$ and $L = M_w^{3\gamma-3}$.

1.3. Jetting model.

Hoath et al. [29] investigated a simple model for determining the polymer’s printability during ejection from the nozzle, the main drop is slowed down through the extensional flow in the connecting fluid linkages. It can be supposed that a drop with density $\rho$ and droplet’s volume $V_{drop}$ is ejected through the nozzle with diameter D. The main drop slows down from speed $U_0$ to final velocity $U_f$ and the velocity of the drop is given by $U = \frac{az}{2t}$.

Supposing that the only forces acting on the drop are from the stress difference in the ligament, so it can be written $\rho V_{drop} \frac{dU}{dt} = -\frac{V_{lig}}{z} \left(\frac{3\mu_0}{2} + GF(A_{zz} - A_{rr})\right)$ (14). From Eq. (10), the configuration tensor components $A_{zz}$ and $A_{rr}$ the extended equations are: $\frac{dA_{zz}}{dt} = \left(\frac{2U}{2z} - \frac{L}{\tau}\right)A_{zz} + \frac{L}{\tau} \frac{E_x}{E_y}$ (15) and $\frac{dA_{rr}}{dt} = -\left(\frac{2U}{2z} + \frac{L}{\tau}\right)A_{rr} + \frac{L}{\tau} \frac{E_x}{E_y}$ (16). These equations are non-dimensional with a relaxation time as the unit of time in the nozzle with diameter D as a length scale. Non-dimensional governing equations for the initial positions ($U = A_{zz} = A_{rr} = 1$), $t = 0$, $r = 1$ and $U = \frac{w l_{0} \mu_{t}}{l_{0}}$ are: $\frac{dA_{zz}}{dt} = -\frac{\mu_{t}}{\mu_{s}} \frac{E_x}{E_y} + GF(A_{zz} - A_{rr})$ (17) where $E^d$ is modified elasticity number and the velocity at time zero is equal to the initial position of $w(l_{0})$. The “Weissenberg” number at time t is given by $w = \frac{Ur}{z} = \frac{U}{z}$ is a decreasing function of time as the length of the ligament z increases. The modified elasticity number (E’) is defined as $E’ = \frac{V_{lig} W_{lig}}{V_{drop} Re}$ (18), Where Re is Reynolds’ number ($Re = \frac{\rho U_0 D}{\mu}$). Generally $\frac{V_{lig}}{V_{drop}}$ is assumed to be 1/4 based on observations in both simulations and experiments of the fluid ejected from the nozzle ends up in the main drop. The dimensionless polymer concentration is given by $C = \frac{G_z}{\mu s}$ which can be extracted from the Zimm scaling around, $W_{lig} M_w^{3\gamma}$ and $C = M_w^{3\gamma-1}$. Hoath, exhibited in this simulation, both the initial positions of the jetting model and the velocity $U_0$ correspond to the time at which the fluid exhausts the nozzle [30]. The equals 17 and 18 can be solved numerically for calculating the ‘optimum jettable concentration’ as a function of molecular weight. Although this model has succeeded in several items, this simple model has a number of limitations including, the model neglects the nozzle geometry, 2-problems due to the flow via the nozzle, and 3- does not take into account the break-off of the ligament from the nozzle. The finite extensibility L can be determined from the ratio of the equilibrium coil to the fully extended length of the polymer so that $L^2 = 3\left(\frac{\sin 3\gamma}{\cos M_{\mu}}\right)^{2(1-\gamma)}$ (19), where $\theta$ is the carbon-carbon bond angle, $j$ is the number of bonds of a monomer unit with molar mass $M_{\mu}$ and $C_{\cos}$ is the characteristic ratio [31]. Hence, for a dilute mono-disperse polymer solution, the FENECR model. Parameters scale with solvent quality factor $\theta$, it can be shown $G = M_w^{3\gamma-2}$, $\tau = M_w^{3\gamma}$ and $L = M_w^{3\gamma-3}$ thus, by using the Zimm model to determine the molecular weight dependence of the relaxation time it can be determined how the maximum jet-able polymer concentration scales with molecular weight during each of the three jetting regimes. These scaling laws are summarized in Table 1.

| Concentration | Regime 1 $M_w^{1-3\gamma}$ | Regime 2 $M_w^{1-2\gamma}$ | Regime 3 $M_w^{1-\gamma}$ |
|---------------|---------------------------|---------------------------|---------------------------|
| $W_{lig}$     | $\mu_{s}$                 | 1                         | $\mu_{t}$                 |
| $l_{0}$       | $\frac{w l_{0} \mu_{t}}{l_{0}}$ | 1                         | $\frac{w l_{0} \mu_{t}}{l_{0}}$ |

1.4. Thermal DOD.

Thermal inkjet printers, work based on via rapidly heating a small amount of ink inside a reservoir with an open nozzle with a resistor attached to a power supply. The ink vaporizes through the heat and consequently creating a bubble which with high pressure (more than one Mega Pascal) causes a wave force inside the fluid of reservoir to exit a droplet via the nozzle. The advantage of this system is the comparatively low cost, as it includes only a resistor and a reservoir, easily fabricated via existing methods with low-cost goods [32, 33]. So, thermal inkjet printers are generally used as household systems, where cost and simple print head replacement are important. The subject related to thermal printers is their limited applicability – generally, inks must be water-based and low-viscosity (less than one cP) to be easily vaporized. It is notable; the high thermal may destroy the ink vaporized, causing damage to the print head. Therefore, Thermal inkjet printers are better-suited for printing of conventional inks for graphics and text (Scheme 3).

1.5. Piezoelectric DOD.

Piezoelectric devices are suitable for a broader range of ink formulations and materials by avoiding thermal printer problems. A mechanical changing of a small ink reservoir induces a pressure wave in the liquid materials, forcing out the droplets. The print head which causes the mechanical deformation is a piezoelectric crystal, which changes shape upon the application of voltage; applying this unique good means that the manufacture of piezoelectric print head is extremely difficult and costly compared to thermal ones. The advantage between piezoelectric print head model with the thermal printer is the ability to which drop size can be controlled. In addition controlling the droplet shape, careful adjustment of peak voltage, and voltage pulse length or voltage-time waveform are the other advantages [34]. The wave form of the piezoelectric inject printing is shown in Fig.1.
1.6. Fluid dynamics & ink ejection.
The fluid dynamics happening during printing is due to the acoustic pressure waves, because of the piezoelectric material, which force droplets out of the nozzles. Each of these items involves unique fluid mechanics. The mechanism effect of the fluid movement inside the ink region for producing a jetting situation was clearly explained by Shield et al which a schematic of their model is shown in Figure 2. [37]. The motion of the ink starts with the application of voltage to the piezoelectric element. Usually, voltages are applied such that the ink cavity enlarges and creating a negative pressure inside it. Consequently producing two negative waves in two opposite directions from the piezoelectric element push out the droplets. These two waves are reflected from the liquid reservoir and the nozzle opening, the first one changing its sign during reflection to a positive acoustic wave and the second one reflecting back as a negative acoustic wave.

Figure 2. Acoustic wave propagation in a piezoelectric nozzle. (A): first voltage rise +V potential contraction, -V pressure Wave, (B): Dwell time and reflection from reservoir and (C): voltage fall –V potential amplification of +V pressure wave jetting. The voltage dropping occurs in the second section of the wave form, producing two positive pressure waves in an opposite orientation. One of these annihilates has been reflected negative pressure, and the other doubles the amplitude of the reflected positive one. The propagating pressure wave forces out a droplet of ink for overcoming the viscosity and tension of surfaces on the ink at the nozzle. The entire process and consequently, the length of a generic jetting waveform are around 20 µs [32]. Due to the speed pressure wave, it will have some bearing on how long this process takes. Therefore waveform length will vary with applied voltages and printer being used.

2. MATERIALS AND METHODS
2.1. Materials for inkjet printing devices.
Although theoretically any liquids and compositions that can be dissolved or dispersed into the inks might be used as a subject in a printer devises, the structures of fluid parameters and film-forming situation limit materials selection. Especially, small dispersed particle size restricts of liquids, colloids polymers, micelle and other nanostructures such as nanotubes or fullerenes can be important for any further studies [38–42]. These materials can be divided into three categories including insulators, conductors and semiconductors. There are other supplementary materials that are very important, and these materials must be considered as part of the printer devices such substrate or electronics sections. Especially, a major material to be considered in a printer devices, is substrate and it must be any conventional rigid process able flexible. Dissolution of dielectric inorganic materials, semiconductors and also metals with solvents, is not generally possible at standard conditions for any printing. In addition conversion of a precursor to the suitable material during/after jetting can be considered, as with AgNO3-based inks producing such as Ag films [43] or sol-gels for ceramics and oxides [44] but the production of sintered or crystalline films requires hydrothermal treatment [45]. A metallic colloid occasionally requires a high temperature after printing or for sintering and any electrical conductivities [41]. In the item of polymers and macromolecules, inkjet depositions of dissolved materials are possible. It is notable; loading of the ink with more than a small concentration of polymers can cause undesirable effects in any droplets formation, particularly the bead-on-a-string effect. Therefore, dispersed particles of either polymers or inorganic compounds which require no aggressive post treatments
present the simplest deposition way. In this review, materials that were functional upon deposition were studied. This means the material was dispersed in the ink by its desired properties such as chemical, thermal, hydrothermal or other behaviors to be applied for inducing functionality in the printer film.

2.2 Conductors.

Electronic printers, applies a passaging of electrons for providing a desired function. In order to transition electrons via a device, a suitable electrode material with high conductivity and low losses in voltage, current, is required. Generally, a set of two electrodes is applied for providing a complete circuit for electrons flowing in a power source. Sometimes, these two electrodes are composed of the same material and in some cases consist of two different materials, due to the electrical position of inkjet printing. Although there are several different conductive materials, only some of them are readily accessible in a form suitable for inkjet printer. The three main categories of these structures are Nano carbon materials, metallic colloids, and conjugated polymers. The two first items are dispersible species, whereas conjugated polymers might be either dispersed or dissolved. Metallic colloids have become extremely common as inkjet-printable materials, and include such conventionally-used electrode materials as Ag [46-48]. Recently in several works, conductivities comparable to bulk amounts have been used with the colloids [49, 50]. Commonly, these methods need a high-temperature curing phase for removing solvent and organic ligands from the nanoparticles, which are used for stabilizing the colloidal suspensions. The solvents and also encapsulating polymers ligands which stabilized the particles in solution prevent sintering from occurring until they are removed. The solvents might be decompose or evaporate at a comparatively low temperature, leading to the consumption of such materials as nitrocellulose, which decomposes around 135°C [51]. During the removal of the cap, the particles are usually still non-conductive, being physically segregated to prevent any effective electron transfer [40, 41]. They are generally then sintered at high temperature for inducing crystal growth and Nano-particle merging. The huge surface energies compared to low volume of these small particles might cause a reduction in melting temperature upwards of 500°C [52,53]. High temperature’s sintering process for the metals and even much higher temperature for the metal oxides, the usual cutoff point for flexible substrates. The colloidal metals and also metal-oxides make excellent and suitable material for inkjet-printed conductive layers, especially on a glass substrate which the high temperatures have not any concern. Therefore, colloidal metal or metal-oxides are acceptable for use in small amounts, but usually only on glass or comparable substrates. Recently, attempts have been done for reducing the sintering’s temperature of these kind materials and opening the novel methods for their use on any flexible substrate. Such as a technique which used include the preparation of a metal-organic Ag precursor rather than nanoparticles with a low temperature [46]; the use of more weakly adsorbent ligand species to cap Ag nanoparticles [54]. Carbon nanostructures including graphene, nanotubes, Nano rods and Nano balls such as fullerene are the other main series of printable electrode materials. Amorphous carbons are intrinsically conductive because of the valence electrons delocalization and covalent C-C “π” bonds. It is notable that conductivity in carbon is often significantly lower than in metals. Electrical conduction in carbon relies on electron transfer along the C-C bonds in a single sheet, while in the metals electrons are delocalized in every orientation within a metallic crystal lattice, providing many adjacent conduction sites. In addition within the Nano carbon structures and tubes there is also vast variation in their conductivities, attributable to changes in the electronic wave vectors of the structure in question. The most commonly inkjet-printing devices are based on Nano carbon species including carbon nanotubes (CNTs), armchair, zigzag and chiral of both single-(SWCNTs) and multi-walled (MWCNTs) as well as fullerene, and graphene. Schematics of these structures are shown in Fig.3. SWCNTs and multi layers of graphene are usually used as inkjet printer electrode’s materials than fullerenes due they can layer into stacked sheets or networks, whereas fullerenes like metallic colloids, have to be packed tightly for allowing electrons to hop among them.

These kind treatments were observed in printed layers of multi wall carbon Nano tubes (MWCNT) [55], where overprinting of successive sheets were sufficient for improving conductivities extremely, as more MWCNTs filled in the network of overlapping conductive paths. Various other carbon materials also successfully printed as electrodes or interconnect in different electronics printers, including thin-film, transistor and field effect transistor [56, 57].

In most categories the surface resistance of CNT and graphene films were still several orders of magnitude higher than that metals. However, carbon material does present a few unique advantages over these conventional materials.

First, the nanostructure allows for a degree of flexibility in inkjet printing. Second, the processing of carbon Nano tube or graphene dispersions do not require high-temperature sintering like metal nanoparticle suspensions. In addition the solvents have to be removed for allowing the compounds for electrical conducting. It is notable, carbon materials will not sinter under atmospheric position regardless of temperature [58]. Surface functionalization of SWCNTs or graphene surfaces with organic groups can be achieved dispersion in several of solvents without
3. RESULTS

3.1. Numerical simulation.

Based on equations in paragraphs 2 & 2.1 the inkjet printing has been simulated with commercialized CFD software (Flow3D). The droplet formations have been done after supposing the structure of the fluid meniscus, while the numerical simulation of drops formation has been done through supposing the initial figure at the tip of the nozzle [87]. Although, the proper simulation of an electrostatic ink jetting can be performed on different kinds of electrostatic printer devices, the volume of fluid (VOF) technique is important method that might be investigated [88, 89].

In some items such as of capillary nozzle type, some researchers have accomplished the simulation on the electro-hydro-dynamics via using VOF method [90-92] using commercialized CFD [93, 94]. Although piezo-actuators are used for generating droplets in most of the conventional inkjet systems, in recent a great deal of research has been going on regarding the electrostatic inkjet systems. The electrostatic inkjet systems along with the forces during the droplet generation process are shown in Fig 4 & Scheme3.

![Figure 4. Forces acting on the ink at the tip of the nozzle.](image)

The electrical voltages are applied as a signal between two electrodes, consequently an intense electrical field is produced which induce the liquid meniscus at the interface. As electrical force becomes greater than the surface tension, the liquid breaks up and droplets are ejected. The size of the droplets is dependent on the shape and size of nozzle. Voltages, distances among the electrodes, and physical chemistry properties of the fluid.

As mentioned in paragraph 2, the Navier-Stokes equation consists of three parts as : \( \rho \frac{du}{dt} = -\nabla P + \eta \Delta^2 u + \rho g \) (20) and for solving the treatment of electrostatic inkjet equations the fluid dynamic and electrical equation must be merged in one formula based on mechanical stress and electrical stress along with the gravitational forces which can be rewritten as: \( \rho \frac{du}{dt} = -\nabla P + \eta \Delta^2 u + \rho g + qE \) (21). The equations of motion were solved numerically using the “Verlet algorithm” [94]. Each time step of calculations was fixed around femto second (10^(-15) s) and cut off radius was fixed of 12Å.

For investigate existence of solid and liquid phases in the system the Lindemann index has been applied [95]:

\[
L_i = \frac{1}{N-1} \sum_{j=1}^{N} \sqrt{\frac{r_{ij}^2}{r_{ij}^2} - \frac{r_{ij}^2}{r_{ij}^2}} \quad \text{and} \quad L = \frac{1}{N} \sum_i L_i
\]

Where \( L_i \) and \( L \) are the Lindemann index of \( i \)th atom and whole particle, respectively. \( < \cdots > \), denotes the average \( T \) over time, \( r_{ij} \) is the distance between two atoms. It is notable, “Lindemann” index equal to 0.1 is a criterion to distinguish solid and liquid phase. If the Lindemann index of an atom or a particle is below 0.1, it is in solid state while the Lindemann index above 0.1 denotes high dynamism liquid phases. It is notable to confirm which the Lindemann indexes reveal the dynamism of atoms. A liquid atom has higher dynamism than solid one. The Lindemann indexes are able to identify the solid or liquid phase during the system is in equilibrium condition. A hexagonal and a triangular particle consists of 2000 and the triangle consists of 1300 silver atoms were designed; and MD program was run for each particle for 40000 time steps for reaching an equilibrium. In this study, hexagonal nanoparticle was applied to exhibit joining in edge-to-side configurations while triangular Nano particle was accomplished to exhibit joining. Triangular silver Nano particle in side-to-side configurations was chosen for side to side joining, because of a simple structure at the edges [97-99]. In addition, the corner atoms are not stable due to the sharp angle of corners; therefore, they are not enough data for showing edge to side joining. So, hexagonal silver nanoparticle has been selected to observe side to edge joining. The distances among nearest points of the particles must be less than the cut off radius of the atoms and not too close to push each other away. In this position, the atoms handle attractive forces on each other and the particles become closer together. The results for some dilute solutions are listed in table.2.

| Solvents  | Density g/cm³ | Viscosity cP= mPa.S | Surface tension dyn/cm² | Dielectric Constant | Particles       |
|----------|---------------|---------------------|-------------------------|-------------------|-----------------|
| Water    | 1.0           | 1.0                 | 71.97                   | 78.54             | No              |
| Isopropanol | 0.785          | 2.86                | 21.7                    | 18.3              | Silver, 20% w/w |
| Hexane   | 0.659         | 0.31                | 18.4                    | 1.89              | Silver, 20% w/w |
| Acetone  | 0.791         | 0.32                | 23.7                    | 20.7              | Silver, 20% w/w |
| Diethyl Ether | 0.706       | 0.24                | 17.0                    | 4.34              | Silver, 20% w/w |
| Ethanol  | 0.789         | 1.07                | 22.27                   | 24.5              | Silver, 20% w/w |
For developing an electrostatic inkjet nozzle, it is needed to investigate the treatment of the droplet generation via different shapes of nozzle. Optimal mesh parameters are estimated and applied for the simulations for droplet diameters for the solvents of table 2 are listed in table 3 and plotted in Figs.5&6.

| Solvents | Electrode position(µm) inside Nozzle |
|----------|-------------------------------------|
| Isopropanol | 20                                  |
| n-Hexane   | 25                                  |
| Acetone    | 20                                  |
| Diethyl ether | 20                                 |
| Ethanol    | 15                                  |

Electrical field simulation of different configuration is several nozzles were accomplished for understanding the relation between applied voltages and droplet diameters. The diameters of the nozzles are kept at 45µm. For the simulation purpose, the dilute solutions ink data was used from Table 3.

Although inkjet printing of polymers have been widely reported, suspension polymers in table 4 were tested for particle size for making sure that it would pass through the printer without significant loss of conductive material. An important concern was the sizes and shapes of the CNTs being added to the polymers ink. By the way, with both single walls- and MWCNTs, 0.2 µm filtration removed a large proportion of the nanotubes, due to the small pore size of the filters relative to the length of the nanotubes (Table 4). In the case of SWCNTs, fewer than ~10%-12% of the nanotubes passed through the filter, although a greater number of the nanotube was able to pass via the print nozzle (without any prior filtration) than were multi wall CNTs. The increased passage via the print-head without any filtrations was likely a result of the relatively large nozzle size of 20-25 µm as compared to the CNTs (5 µm length), and the low concentration of the CNTs. Passage of the configuration of electrode changes. The polymers/CNT ink, conductivities of inkjet-printed indicates that via using single wall carbon nanotubes (SWCNTs) or multi wall carbon nanotubes (MWCNTs) are not only a function of the conductivity of its constituents but also is dependent on the jetting characteristics. Optimizing viscosity and surface tension are needed both for acceptable jetting and for maximizing the connectivity.

4. CONCLUSIONS

Different voltages at 50 kHz frequency were applied to check the droplet behavior for dilute solvents and dilute polymer solutions. As shown in both curves of dilute polymer and solvents, the droplets diameter are decreasing as the voltage increases. Via comparing the graph of droplet generation for both cases, the droplets diameter changed between 10-90 nm dilute solvents and between 40-140 nm for dilute polymer solutions in the range of 1-8 kV, respectively. This exhibits that the droplet size changes as the configuration of electrode changes. The polymers/CNT ink, conductivities of inkjet-printed indicates that via using single wall carbon nanotubes (SWCNTs) or multi wall carbon nanotubes (MWCNTs) are not only a function of the conductivity of its constituents but also is dependent on the jetting characteristics. Optimizing viscosity and surface tension are needed both for acceptable jetting and for maximizing the connectivity.

5. REFERENCES

1. Zips, S.; Grob, L.; Rinklin, P.; Terkan, K.; Fully Printed µ–Needle Electrode Array from Conductive Polymer Ink for Bioelectronic Applications. ACS Applied Materials & Interfaces 2019, 11 (36) , 32778-32786. https://doi.org/10.1021/acsami.9b11774.

2. Hartmann, M.; Hardt, S.; Stability of Evaporating Droplets on Chemically Patterned Surfaces. Langmuir 2019, 35 (14), 4868-4875. https://doi.org/10.1021/acs.langmuir.9b00172

3. Hoth, C.N.; ChouliS, A.A.; Schilinsky, P.; Brabec, C.J. High Photovoltaic Performance of Inkjet Printed Polymer: Fullerene Blends. Adv. Mater. 2007, 19, 3973–3978. https://doi.org/10.1002/adma.200609011

4. Liu, Q.; Orme, M. High precision solder printing technology and the state-of-the-art. J. Mater. Proc. Tech. 2001, 115, 271–283. https://doi.org/10.1016/S0924-0136(01)00740-3.

5. Crowley, K.; O’Malley, E.; Morrin, A.; Smyth, M.R.; Killard, A.J. An aqueous ammonia sensor based on an inkjet-printed polyaniline nanoparticle-modified electrode. Analyst 2008, 133, 391–399. https://doi.org/10.1039/B716154A.

6. Koo, H.S.; Chen, M.; Pan, P.C. LCD-based color filter films fabricated by a pigment-based colorant photo resist inks and printing technology. Thin Solid Films 2006, 515, 896-901. https://doi.org/10.1016/j.tsf.2006.07.159.

7. Meruga, J.M.; Cross, W.M.; Petersen, J.B.; May, P.S.; Baride, A.; Cessac, K.; Kellar, J.J.; Stable Inks Containing Upconverting Nanoparticles Based on an Oil-in-Water Nanoemulsion. Langmuir 2018, 34 (4), 1535-1541. https://doi.org/10.1021/acs.langmuir.7b03415.
8. Singh, M.; Haverinen, H.M.; Dhagat, P.; Jabbour, G.E. Inkjet printing- Process and its application. Adv. Mater. 2010, 22, 673–685. https://doi.org/10.1002/adma.200901141.
9. Rao, A.; Long, H.; Trochiniczky, A.H.; Pham, T.; Zettl, A.; Carraro, C.; Maboudian, R.; In Situ Localized Growth of Metal Oxide Hollow Sphere Array on Microheater Platform for Sensitive, Ultra-Fast Gas Sensing. ACS Applied Materials & Interfaces 2017, 9 (3), 2634-2641. https://doi.org/10.1021/acsami.6b12677.
10. Hebner, T.R.; Wu, C.C.; Marcy, D.; Lu, M.H.; Strum, J.C. Ink-jet printing of doped polymers for organic light emitting devices. Appl. Phys. Lett. 1998, 72, 519–521, https://doi.org/10.1063/1.120807.
11. Yamaguchi, K.; Sakai, K.; Yamanaka, T.; Hirayama, T. Generation of three-dimensional micro structure using metal jet. Precision Eng 2000, 24, 2–8. https://doi.org/10.1016/S0141-6359(99)00015-X.
12. Bogy, D.B.; Shine, S.J.; Talke, F.E. Finite difference solution of the Cosserat fluid jet equations. J. Comput. Phys. 1980, 38, 294–326, https://doi.org/10.1016/0021-9991(80)90151-5.
13. Secor,E.B.; Gao, T.Z.; Islam, A.E Rao, R.; Wallace,S.G.; Zhu, J.; Putz, K.W.; Maruyama, B.; Hersam, M.C.; Enhanced Conductivity, Adhesion, and Environmental Stability of Printed Graphene Inks with Nitrocellulose. Chemistry of Materials 2017, 29 (5), 2332-2340. https://doi.org/10.1021/acs.chemmater.7b00029.
14. Asai, A. Three-Dimensional Calculation of Bubble Growth and Drop Ejection in a Bubble Jet Printer. J. Fluids Eng. 1992, 114, 638–641, https://doi.org/10.1115/1.2910079.
15. Liou, T.M.; Shih, K.C.; Chau, S.W.; Chen, S.C. Three-dimensional simulations of the droplet formation during the inkjet printing process. Int. Comm. Heat Mass Transfer 2002, 29, 1109–1118, https://doi.org/10.1016/S0735-1933(02)00439-6.
16. Richter, L.J.; DeLongchamp, D.M.; Amsamian, A. Morphology Development in Solution-Processed Functional Organic Blend Films: An In Situ Viewpoint. Chemical Reviews 2017, 117 (9), 6332-6366. https://doi.org/10.1021/acs.chemrev.6b00618.
17. Holdeman, J.T. A Hermite finite element method for incompressible fluid flow. Int. J. Numer. Meth. Fluids 2010, 64, 376–408, https://doi.org/10.1002/tdf.2154.
18. Holdeman, J.T.; Kim, J.W. Computation of incompressible thermal flows using Hermite finite elements. Comput. Meth. Appl. Mech. Eng. 2010, 199, 49–52, 3297–3304, https://doi.org/10.1016/j.cma.2010.06.036.
19. Kumar, A.; Raj, R.; Droplets on Microdecorated Surfaces: Evolution of the Polygonal Contact Line. Langmuir 2017, 33 (19), 4854-4862. https://doi.org/10.1021/acs.langmuir.7b00559.
20. Nunes, P.S.; Ohlsson, P.D.; Ordeig, O.; Kutter, J.P. Cyclic olefin polymers: Emerging materials for lab-on-a-chip applications. Microfluid. Nanofluid. 2010, 9, 145–161, https://doi.org/10.1007/s10404-010-0605-4.
21. Hirt, C.W.; Nichols, B.D.; Volume of Fluid (VOF) method for the dynamics of free boundaries. J. Comput. Phys. 1981, 39, 201–225, https://doi.org/10.1016/0021-9991(81)90145-5.
22. Rahman, R.M.; Waghmare, P.R. Double-Emulsion Drop Evaporation and Formation of a Daughter Droplet. Langmuir 2019, 35 (12), 4403-4411. https://doi.org/10.1021/acs.langmuir.8b03862.
23. Elton, E.S.; Tibrewala, Y.V.; William D. Ristenpart. Statistical Analysis of Droplet Charge Acquired during Contact with Electrodes in Strong Electric Fields. Langmuir 2019, 35 (11), 3937-3948. https://doi.org/10.1021/acs.langmuir.8b04254.
52. Meixner, R.; Cibis, D.; Krueger, K.; Goebel, H. Characterization of polymer inks for drop-on-demand printing systems. Microsys. Techn. 2008, 14, 1137, https://doi.org/10.1007/s00542-008-0639-7.

53. Liu, Z.; Su, Y.; Varahramyan, K. Inkjet-printed silver conductors using silver nitrate ink and their electrical contacts with conducting polymers. Thin Solid Films 2005, 478, 275, https://doi.org/10.1016/j.tsf.2004.11.077.

54. Zhou, Z.; Yang, Z.; Yuan, Q. Metal nanoparticles as low conversion temperature films for continuous inkjet printing synthesized by mechanical mixing and sol-gel methods. Trans. Nonferrous Met. Soc. China 2008, 18, 150, https://doi.org/10.1016/S1003-6326(08)60027-8.

55. Zeng, J.; Lin, C.; Li, J.; Li, K. Low-temperature preparation of barium titanate thin films by a novel sol-gel-hydrothermal method. Materials Letters 1999, 38, 112, https://doi.org/10.1016/S0167-577X(98)00142-6.

56. Dearden, A.; Smith, P.; Shin, D.; Reis, N.; Derby, B.; O’Brien, P. A low curing temperature silver ink for use in ink-jet printing and subsequent production of conductive tracks. Macromol. Rapid Comm. 2005, 26, 315, http://doi.org/10.1002/marc.200400445.

57. Wu, Y.; Li, Y.; Ong, B. A simple and efficient approach to a printable silver conductor for printed electronics. J. Amer. Chem. Soc. 2007, 129, 1862, https://doi.org/10.1021/ja067596w.

58. Jeong, M.; Byeon, C.; Cha, O.; Jeong, H.; Han, J.; Choi, Y.; An, K.; Oh, K.; Kim, K.; Lee, Y. Purity measurement of single-walled carbon nanotubes by UV-vis-nIR absorption spectroscopy and thermogravimetric analysis. Nano Brief Rep. Rev. 2008, 3, 101, https://doi.org/10.1142/S1793292008000885.

59. Jeong, S.; Song, H.; Lee, W.; Choi, Y.; Ryu, B. Preparation of aqueous Ag InK with long-term dispersion stability and its inkjet printing for fabricating conductive tracks on a polyimide film. J. App. Phys. 2010, 108, 1, https://doi.org/10.1063/1.3511686.

60. Nguyen, B.; Gautrot, J.; Nguyen, M.; Zhu, X. Nitrocellulose-stabilized silver nanoparticles as low conversion temperature precursors useful for inkjet printer electronics. J. Mater. Chem. 2007, 17, 1725-1730, https://doi.org/10.1039/B616446C.

61. Nguyen, T.; Yee, R.; Schwartz, B. Solution processing of conjugated polymers: the effects of polymer solubility on the morphology and electronics properties of semiconductor printing polymers. J. Photochem. Photobiol. A: Chem. 2001, 144, 21, https://doi.org/10.1016/S1010-6030(01)00377-X.

62. Huang, D.; Liao, F.; Moleasa, S.; Redinger, D.; Subramanian, V. Plastic-compatible lowresistance printable gold nanoparticle conductors for flexible electronics. J. Electrochem. Soc. 2003, 150, 412, https://doi.org/10.1149/1.1582466.

63. Huang, L.; Huang, Y.; Liang, J.; Wan, X.; Chen, Y. Graphene-based conducting inks for direct inkjet printing of flexible conductive patterns and their applications in electric circuits and chemical sensors. Nano Res. 2011, 4, 675, https://doi.org/10.1007/s12274-011-0123-z.

64. Perelaer, J.; de Laat, A.; Hendriks, C.; Schubert, U. Inkjet-printed silver tracks: low temperature curing and thermal stability investigation. J. Mater. Chem. 2008, 18, 3209, https://doi.org/10.1039/B720032C.
Monajjemi, M.; Ghiasi, R.; Seyed Sadjadi, M.A. Metal-stabilized rare tautomers: N4 metalated cytosine (M = Li, Na, K, Rb and Cs), theoretical views. Applied Organometallic Chemistry 2003, 17, 635-640, https://doi.org/10.1002/aoc.469.

70. Ilkhani, A.R.; Monajjemi, M. The pseudo Jahn-Teller effect of puckering in pentamonic unsaturated rings C, A, N, P, As, E=H, F, Cl. Computational and Theoretical Chemistry 2015, 1074, 19-25, http://dx.doi.org/10.1016%2Fj.comptc.2015.10.006.

71. Monajjemi, M. Non-covalent attraction of B N and repulsion of B N in the B N ring: a quantum rotary due to an external field. Theoretical Chemistry Accounts 2015, 134, 1-22, https://doi.org/10.1007/s00214-015-1668-9.

72. Monajjemi, M.; Naderi, F.; Mollaamin, F.; Khaleghian, M. Drug design outlook by calculation of second virial coefficient criterion for nano studies. Molecules 2015, 20, 21636-21657, https://doi.org/10.3390/molecules201219769.

73. Monajjemi, M.; Mohammadian,N.T. S-NICS: An aromaticity criterion for nano molecules. Journal of Computational and Theoretical Nanoscience 2015, 12, 4895-4914, https://doi.org/10.1166/jctn.2015.4458.

74. Monajjemi, M.; Ketabi, S.; Hashemian Zadeh, M.; Amiri, A. Simulation of DNA bases in water: Comparison of the Monte Carlo algorithm with molecular mechanics force fields. Biochemistry (Moscow) 2006, 71 (SUPPL. 1), S1-S8.

75. Monajjemi, M.; Lee, V.S.; Khaleghian, M.; Monajjemi, F. Theoretical Description of Electromagnetic Nonbonded Interactions of Radical, Cationic, and Anionic NH2BHNBHNI2 inside of the B18N18 Nanoring. J. Phys. Chem C 2010, 114, 15315, https://doi.org/10.1021/jp104274z.

77. Monajjemi, M.; Mobbs, J.E. A New Generation of BnNa Rings as a Supplement to Boron Nitride Tubes and Cages. J. Phys. Chem. A 2013, 117, 1670-1684, http://dx.doi.org/10.1021/jp312073q.

78. Monajjemi, M.; Mobbs, J.E. Non bonded interaction between BnNn (stator) and BN B (rotor) systems: A quantum rotation in IR region. Chemical Physics 2013, 425, 29-45, https://doi.org/10.1016/j.chemphys.2013.07.014.

79. Monajjemi, M.; Robert, W.J.; Mobbs, J.E. NMR contour maps as a new parameter of carboxyl's OH groups in amino acids recognition: A reason of tRNA–amino acid conjugation. Chemical Physics 2014, 433, 1-11, https://doi.org/10.1016/j.chemicalphysics.2014.01.017.

80. Monajjemi, M. Quantum investigation of non-bonded interaction between the B15N15 ring and BH2NBH2 (radical, cation, and anion) systems: a nano moleculararmor. Struct Chem 2012, 23, 551–580, http://dx.doi.org/10.1007/s11224-011-9895-8.

81. Monajjemi, M. Metal-doped graphene layers composed with boron nitride–graphene as an insulator: a nano-capacitor. Journal of Molecular Modeling 2014, 20, 2507, https://doi.org/10.1007/s00894-014-2507-y.

82. Monajjemi, M. Graphene/(h-BN)n/X-doped raphene as anode material in lithium ion batteries (X = Li, Be, B AND N). Macedonian Journal of Chemistry and Chemical Engineering 2017, 36, 101–118, http://dx.doi.org/10.2450/njmccce.2017.1134.

83. Monajjemi, M. Cell membrane causes the lipid bilayers to behave as variable capacitors: A resonance with self-induction of helical proteins. Biophysical Chemistry 2015, 207, 114-127, https://doi.org/10.1016/j.bpc.2015.10.003.

84. Monajjemi, M. Study of CDS+ Ions and Deuterated Variants (CHx(D5-x)++): An Artefactual Rotation. Russian Journal of...
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