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# Spreading of the nanofluid triple line in ink jet printed electronics tracks☆

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ABSTRACT

One of the next avenues for Additive Manufacturing to develop is that of multi-material deposition in order to add functionality to the already complex geometries that are capable of being manufactured. However, for electronic applications the fidelity of the deposited electronic tracks is of utmost importance. The purpose of this study was to investigate the effects of solid surface tensions, $\sigma_{sg} - \sigma_{sl}$, on the quality of printed lines, using 30–40 nm silver nanofluid ink. The solid surface tensions of silver ink on glass and polytetrafluoroethylene (PTFE) substrates were determined theoretically, knowing characteristics of droplet. Meanwhile, a Dimatix printer with nozzles of size of 21.5 μm was used to print conductive lines on smooth glass and PTFE substrates. The printed lines on glass were observed to be continuous with high quality of triple line, which was attributed to the high solid surface tensions of silver nanofluid ink on glass substrates. The solid surface tensions of silver nanofluid ink were relatively low on PTFE, as results the printed lines were discontinuous. The solid surface tensions were introduced as a reliable criterion to predict the printability of nanofluids. The distribution of silver nanoparticles and layering phenomenon in silver nanofluid triple region on glass substrate was clearly observed, using environmental scanning electron microscopy (ESEM) for the first time. In addition to disjoining pressure, the size of droplet and affinity of nanofluid for substrate were observed to have important influences on spreading of nanoparticles in triple region.



## 1. Introduction

Additive Manufacturing (AM) has reached a point where the development of complex shapes and topologies are now possible in materials that many industrial users can or are beginning to accept. For some the next paradigm of AM is to develop systems and materials that are capable of complex 3D shape with the addition of multiple materials contemporaneously for the addition of function. One such functionality is to add the ability to 'thread' electronics throughout a 3D space encased within dielectric material, however for these materials, normally conductive nanoparticle inks, to have success high fidelity of these tracks is key to their performance. The printing of conductive nanoparticles is attractive due to their potential applications in printed electronic circuits. The direct deposition of conductive lines has a significant influence on the cost and manufacturing of micro devices.

It is also important to maximize the conductivity or minimize the resistance of printed tracks. For a given resistivity, the resistance of a printed track depends on its cross sectional area. Engineering of surface wettability [1] and the behavior of the triple line (triple line is a line that gas, solid and liquid meet each other) are the most effective methods to manipulate the cross sectional area of a printed line. Recently, microstructuring of the substrates has been suggested to modify the wettability and cross sectional area of the printed lines, using nanofluid inks [1].

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**Nomenclature**

| | |
|---|---|
| $g$ | Acceleration of gravity [$m/s^2$] |
| $R_o$ | Radius of curvature at apex [$m$] |
| $R_1$,$R_2$ | Radius of curvature [$m$] |
| $r_d$ | Radius of contact line [$m$] |
| $V$ | Volume [$m^3$] |
| *Greek Symbols* | |
| $\delta$ | Height of apex [$m$] |
| $\theta_e$ | Equilibrium contact angle [*Deg.*] |
| $\rho_l$ | Liquid density [$kg/m^3$] |
| $\rho_g$ | Gas density [$kg/m^3$] |
| $\sigma_{lg}$ | Liquid-gas surface tension [$N/m$] |
| $\sigma_{sg}$ | Solid-gas surface tension [$N/m$] |
| $\sigma_{sl}$ | Solid-liquid surface tension [$N/m$] |
| $\sigma_{lg\,n}$ | Liquid-gas surface tension of nanofluids [$N/m$] |

Practically, the behavior of the triple line or wettability mainly depends on the force balance between liquid-gas, $\sigma_{lg}$, and solid surface tensions, $\sigma_{sg}-\sigma_{sl}$. In general, for a given injected liquid volume, the triple line moves toward the liquid phase as solid surface tensions, $\sigma_{sg}-\sigma_{sl}$, decreases and consequently it reduces the contact area (between liquid and solid surface) and therefore increases the height buildup of the nanoparticle ink line thus increasing the cross sectional area and the volume of deposited nanoparticles, this can consequently decreases the resistance of the printed line. It is therefore, essential to understand how concentration and characteristics of nanoparticles, base liquid, feasible nanoparticle coating, possible surfactant and the physical properties of the nanofluid affect the behavior of the triple line and hence the printing characteristics of a nanofluid ink on a particular substrate. The waviness or quality of the triple line [2,3] will be affected by characteristics of the solid substrate [4], distribution of nanoparticles in the triple region [5–7], force balance between liquid-gas [8–10] and solid surface tensions [11,12]. The liquid-gas and solid surface tensions play a significant role in the behavior of the triple line. Normally, the liquid-gas surface tension needs to remain within a certain range (0.028–0.033 N/m at operating temperature) to be printable using conventional inkjet printers. As a result, the force balance and quality of the triple line mainly depends on the solid surface tensions. The quality of the triple line has a significant influence on the resolution and resistance of printed lines and hence accurate characterization of the quality of the triple line is an important step in the development of a predictive capability for (3D) printing conductive lines.

In this study, the solid surface tensions are predicted, knowing the asymptotic contact angle for a solid-fluid pair, and the relations between solid surface tensions, printability of conductive nanoparticles and distribution of nanoparticles in the triple region are discussed. In addition, the distribution of nanoparticles and the layering phenomenon are examined for nanofluid drops on glass, polytetrofluoroethylene (PTFE) and stainless steel substrates using the environmental scanning electron microscopy (ESEM) technique for the first time.

## 2. The behavior of nanofluid triple lines

### 2.1. General behavior of triple lines

The liquid-gas, $\sigma_{lg}$, solid-liquid, $\sigma_{sl}$, and solid-gas, $\sigma_{sg}$ surface tensions are major effective forces on the triple line. The schematic of liquid-gas and solid surface tensions, $\sigma_{sg}-\sigma_{sl}$, for droplets is given in Fig. 1. The liquid-gas surface tension is available for most chemicals however the solid-liquid and solid-gas surface tensions cannot be found easily. A couple correlations have been used to obtain the solid surface tensions [13,14], such as Berthelot's combining rule [15], the modified Berthelot's rule [16], the alternative formulation [17,18], and the equation of state formulation [19,20]. The correlations have been compared with each other for some materials [14]. For a given liquid-gas surface tension, the solid surface tensions can play a key role in the behavior of the triple line. It was observed that the radius of the triple line expands towards the gas phase as the solid surface tension increases [3].

Young equation, $\sigma_{lg}\cos\theta_e=\sigma_{sg}-\sigma_{sl}$, demonstrates the force balance between liquid-gas, $\sigma_{lg}$, and solid surface tensions, $\sigma_{sg}-\sigma_{sl}$, at the triple line, where the equilibrium contact angle, $\theta_e$, is size independent (see Fig. 1). The Young equation has several limitations and has never been verified experimentally for axisymmetric droplets. The application of the Young equation is limited to ideal substrates [13,21] and contact angle is size independent [12,22] such as long droplets [12]. In the case of an axisymmetric droplet, one side of the Young equation, $\sigma_{lg}\cos\theta_e$, is size dependent while the other side of the equation, $\sigma_{sg}-\sigma_{sl}$, contains physical properties which makes the equation inconsistent.

It has been observed that the droplet contact angle varies under different gravitational accelerations based on the parabolic flight campaign [23] and drop tower methods [24]. It has been observed that droplet contact angle increases as the effect of gravity decreases. As the gravitational acceleration decreases to zero, the droplet shape gradually changes to a spherical cap. The droplet contact angle under zero gravity has been defined as the asymptotic contact angle, $\theta_s$ [11,12]. The asymptotic contact angle is only dependent on the physical properties and interactions between gas, liquid and solid at the triple line, and is a unique criterion to measure surface wettability or the effects of nanoparticles on surface wettability.

The contact angle has been observed to change with droplet volume [12,13,22], so the concept of line tension has been employed to explain the variation of droplet contact angle with volume. The line tension has a significant role in the effect of droplet size on contact angle, leading to a modified Young equation, $\frac{\sigma}{r_d}+\sigma_{lg}\cos\theta_e=\sigma_{sg}-\sigma_{sl}$ß, that considers the effect of the line tension, $\sigma$. The value of line tension has been obtained experimentally [13,25] and theoretically [26,27]. The line tension operates to expand the length of the triple line when it is negative and vice versa [25]. Most probably, the line tension would be zero under zero gravity conditions, since droplet contact angle, liquid-gas and solid surface tensions are constant while the radius of triple line would change by volume. It has been also reported that (a) the line tension decreases as wettability increases and likely vanishes at super-wetting [28], (b) the line tension is a function of the liquid material [28–31], (c) there are large uncertainties, associated with determining both magnitude and sign of the line tension [13,32]. The accurate measurement of line tension is difficult, because (I) its value is small, (II) lack of accurate measurement techniques, (III) possible contamination in triple line, (IV) lack of accurate modeling techniques and (V) the effect of various parameters on line tension is not well recognized

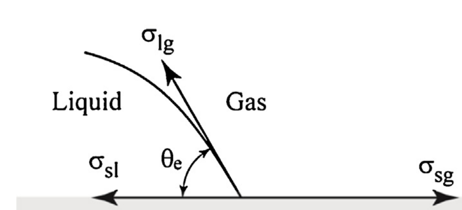


**Fig. 1.** Schematic of forces between liquid-gas and solid surface tensions at the droplet triple line.