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Effect of viscosity, electrical conductivity, and surface tension on direct-current-pulsed drop-on-demand electrohydrodynamic printing frequency

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Experiments were conducted to measure the performance of direct-current-pulsed electrohydrodynamic drop formation as a function of liquid viscosity, electrical conductivity, and surface tension. While hydrodynamic and charge relaxation times and Taylor cone formation frequencies suggest theoretical drop-generation frequencies well in excess of 100 Hz, we show that it is impossible to produce more than 50 drops per second with performance decreasing as viscosity increased or electrical conductivity decreased (and not a significant function of surface tension). Instead of relying on relaxation-time calculations to predict the maximum, reliable drop-production frequency, a dimensionless coefficient that is a function of viscosity and electrical conductivity is proposed to estimate the fulcrum frequency. © *2014 AIP Publishing LLC*.
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Recently, direct printing has been used in bio applications[1] and also to manufacture electronic devices,[2] solar cells,[3] and LCD displays.[4] Electrohydrodynamic (EHD) inkjet printing is one of the most promising high-resolution printing techniques because electrical forces facilitate accuracies down to several tens of nanometers.[5,6] Printing speed and dot size are controlled through application of precise voltages to the inkjet nozzle.[7] However, there is a limit to the response of ink ejection to the voltage signal and also to the minimum drop size.[8] To improve the quality of high-frequency drop-on-demand (DOD) space printing, operating conditions and ink properties need to be fully characterized. EHD DOD inkjet printing performance is primarily a function of viscosity,[7] applied voltage,[9] and pulse interval.[10] Lee *et al*. show that the applied voltage and duration affect both drop size and overall printing quality.[11] According to Mishra *et al*., application of a 1-kH DC voltage only generated drops at a frequency of 60 Hz, which clearly does not equate to DOD.[10] At the meniscus of the ink at the nozzle tip, electrical forces and surface tension balance.[12] Stachewicz *et al*. explained that the discrepancy between applied voltage frequency and drop generation is a function of the ink's electrical conductivity and viscosity.[13,14] Specifically, higher electrical conductivity and lower viscosity of the ink improve the response to the applied voltage. This effort characterizes the effects of liquid properties (electrical conductivity, viscosity, and surface tension) on EHD inkjet printing. In particular, we focus on improving high-frequency DOD printing by optimizing liquid properties.

For a fixed nozzle diameter, hydrodynamic relaxation time is linearly proportional to ink viscosity,[15]

$$\tau_H = \frac{\mu r}{\sigma}, \tag{1}$$

where r is the outer radius of the capillary and μ and σ are the viscosity and surface tension of liquid, respectively. The ratio of σ/μ describes the characteristic velocity of the jet.[12]

Charge transport, or charge relaxation time, is inversely proportional to the electrical conductivity of the liquid[16]

$$\tau_e = \frac{\varepsilon_r \varepsilon_o}{K}, \tag{2}$$

where ε_r is relative electrical permittivity, ε_o is vacuum permittivity (8.8542×10^{-12} F/m), and K is electrical conductivity.

The preceding equations show that droplet formation times are decreased with lower viscosities and higher electrical conductivities or surface tensions of the ink.

Figure 1 is a schematic of the experimental setup. Voltage is controlled with a multi-function synthesizer (WF 1973, NF corporation) and amplified over 1000-fold by a TREK 10/40 A voltage amplifier. The amplified voltage is applied to a stainless-steel nozzle (Nordson EFD, inner and outer diameters of 0.84 and 1.27 mm, respectively). Property-controlled liquids are supplied from a syringe pump (KDS legato 100, KD Scientific Inc.) at a fixed flow rate of 0.2 ml/hr. The rectangular voltage pulse is fully defined by its magnitude (V) and duration (τ) (note: no voltage bias). For consistent inkjet printing, the voltage is fixed and the duration is set to a minimum value upon printing ($\tau = \tau_{min} = 0.2 \sim 4.9$ ms). The fluid viscosity is controlled by mixing glycerin (DUKSAN chemical) with DI water. Nitric acid and surfactant (Triton X-100, Sigma Aldrich) are added to vary the electrical conductivity and surface tension of the liquid, respectively. The viscosity, electrical conductivity, and surface tension of each liquid are measured at room temperature using a viscometer (LVDV-I+ CP, Brookfield), an electrical

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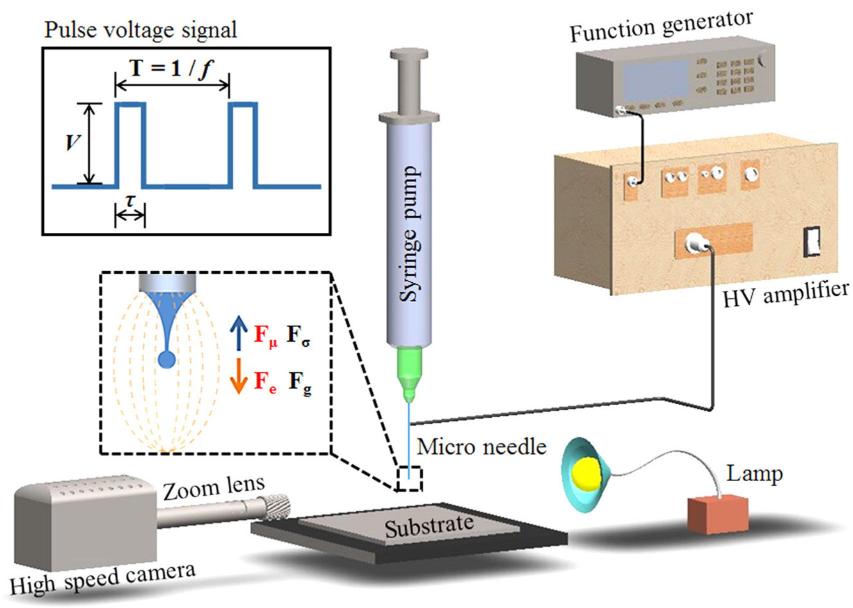

FIG. 1. Schematic of the experimental setup for the EHD printing system (T is the pulse interval time, f is the voltage frequency, V is the applied voltage, τ is the pulse duration, F_μ is the viscous force, F_σ is the surface tension force, F_e is the electric field force, and F_g is gravity force).

conductivity meter (HI 98360, Hanna Instrument), and a surface-tension meter (DST 60 A, Surface & Electro-Optics Co., Ltd), respectively. Table I summarizes liquid properties. Inkjet droplets are visualized using a high-speed camera (Phantom 7.3, Vision Research, Inc.), zoom lens (1.56 mm/pixel), and halogen lamp (250 W). The distance between nozzle and substrate is fixed at $L = 10$ mm and a polished stainless steel substrate acts as the voltage ground.

Figures 2(a) and 2(b) illustrate how the voltage magnitude and duration change with applied frequency for various liquids. From Figure 2(a), the pulse duration (filled symbols) increases with viscosity at fixed electrical conductivity and surface tension ($K = 500\,\mu$S/cm and $\sigma = 64$ mN/m). From Figure 2(b), the pulse duration increases with decreasing electrical conductivity for fixed viscosity ($\mu = 3.32$ mPa s) and surface tension ($\sigma = 64$ mN/m). These experimental trends agree with what Eqs. (1) and (2) predict. Liquid responds faster when it has a lower viscosity and a higher electrical conductivity. Practically, the linear relation between f_{pulse} and τ breaks down at a certain point because of the fluid's inability to respond exactly to the applied frequency; fluid response time is finite.

Note that no trend was observed while varying the surface tension. In principle, the liquid response time should decrease with increasing surface tension; see Eq. (1). Although surface tension varied from 31 to 64 mN/m, there was no discernible effect on τ over investigated range of σ.

Figure 3 shows the result of DOD performance as a function of viscosity, electrical conductivity, and surface tension. Perfect DOD means that pulsed voltage frequency and drop generation rate (frequency) match (solid black line). Drop generation frequencies deviate from the pulsed voltage frequency upon reaching a liquid-property-dependent threshold. For the least viscous fluid ($\mu = 2.73$ mPa s, green symbols), drop generation rate follows the DOD line up to a voltage frequency of 40 Hz. Above this frequency, drop generation does not keep pace with the applied voltage frequency and actually deceases above 50 Hz. The highest voltage frequency that still yields perfect DOD is called the fulcrum frequency, f_c. The Figure 3(a) inset illustrates how f_c decreases as the viscosity increases. As depicted in the inset of Figure 3(a), f_c is about inversely proportional to the hydrodynamic relaxation time ($\tau_H \sim \mu^{-1}$).

Figure 3(b) shows how the drop generation frequency varies with electrical conductivity. Here, DOD performance is a function of the electrical conductivity, which is inversely proportional to the electrical relaxation time ($\tau_e \sim K^{-1}$) and f_c decreases as the electrical relaxation time increases. The faster transport of electrons through the liquid improves the response of the electric force on the drop. Decreasing the

TABLE I. Properties of EHD liquids (Density, $\rho = 1100 \pm 30\,\mathrm{kg/m^3}$).

μ (mPa s)	K (μS/cm)	σ (mN/m)	τ_H (s)	τ_e (s)	δ_m
2.73	500	64	27.1×10^{-6}	0.013×10^{-6}	0.85
3.32			32.9×10^{-6}		0.69
5.60			55.6×10^{-6}		0.41
3.32	16 500	64	32.9×10^{-6}	0.39×10^{-9}	0.22
	50			0.13×10^{-6}	1.50
3.32	500	31 (0.01 wt. %)	67.9×10^{-6}		0.69
		46 (0.001 wt. %)	45.8×10^{-6}	0.013×10^{-6}	

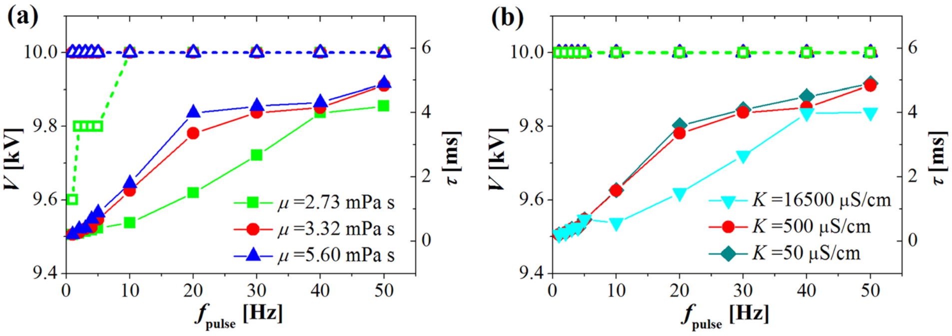

FIG. 2. Voltage (open symbols) and duration (filled symbols) as a function of applied pulse frequency are presented as a function of (a) viscosity with fixed $K = 500\,\mu$S/cm and $\sigma = 64$ mN/m and (b) electrical conductivity with fixed $\mu = 3.32$ mPa s and $\sigma = 64$ mN/m.

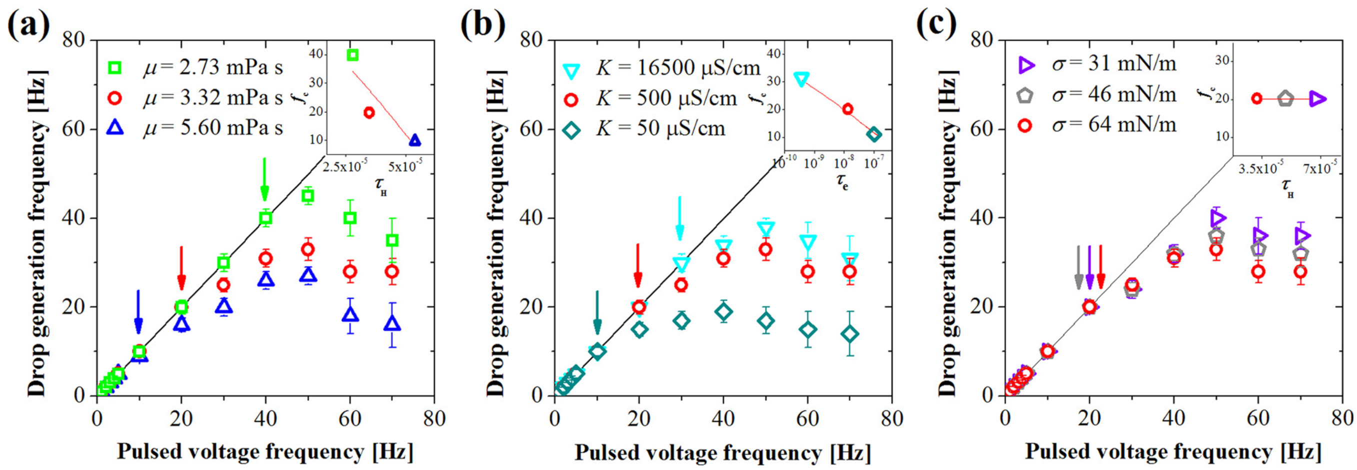

FIG. 3. Correlation between droplet generation and voltage frequency due to (a) varying viscosity for fixed $K = 500\,\mu$S/cm and $\sigma = 64$ mN/m, (b) varying electrical conductivity for fixed $\mu = 3.32$ mPa s and $\sigma = 64$ mN/m, and (c) varying surface tension for fixed $K = 500\,\mu$S/cm and $\mu = 3.32$ mPa s.

viscosity has a more pronounced effect on DOD performance than does increasing the electrical conductivity. Specifically, f_c increases from 10 to 40 Hz upon halving the viscosity. In contrast, increasing electrical conductivity by a factor of 330 from 50 to 16 500 μS/cm increases f_c from 10 to 30 Hz.

Figure 3(c) shows the effect of surface tension on DOD performance for various pulsed voltage frequencies. The surface tension is adjusted to 31, 46, and 64 mN/m by adding surfactant at 0.01, 0.001, and 0 wt. %, respectively (Table I). Such a small amount of surfactant does not significantly affect the viscosity or the electrical conductivity. At voltage frequencies above f_c, drop-generation frequency increases as the surface tension decreases from 64 to 31 mN/m with a peak drop-generation frequency at a 50-Hz voltage frequency, similar to the maxima when varying viscosity and electrical conductivity. According to Eq. (1), the hydrodynamic relaxation time should decrease as the surface tension increases ($\tau_H \sim \sigma^{-1}$), yielding a drop-generation frequency that increases with surface tension. The reason why drop-generation frequency is not proportional to the surface tension can be explained by balancing forces[9] such that $F_g + F_e = F_\sigma$, where F_g is gravity force, F_σ is surface tension force, and F_e is electric-field force. Stable DOD performance is achieved when the above forces are balanced. However, when the downward forces (F_g and F_e) exceed the upward force (e.g., high electrical conductivity), the liquid meniscus breaks up to form a drop and the drop-generation frequency varies with K as illustrated in Figure 3(b). On the contrary, when the upward force (F_σ) increases, the meniscus is stronger with the liquid more able to resist forming drops as shown in Figure 3(c). Although the reaction speed of a liquid should increase as the hydrodynamic relaxation time decreases, the drop-generation frequency actually decreases at higher applied voltage frequencies because increased surface tension inhibits droplets from being ejected from the nozzle. This highlights a discrepancy between using the relaxation time to estimate DOD frequencies and the actual physics of the system where σ inhibits drop formation.

Figure 4 compares the measured f_c as a function of the relative changes of properties of the investigated fluids. Fulcrum frequency is a strong function of μ, a weaker function of K,

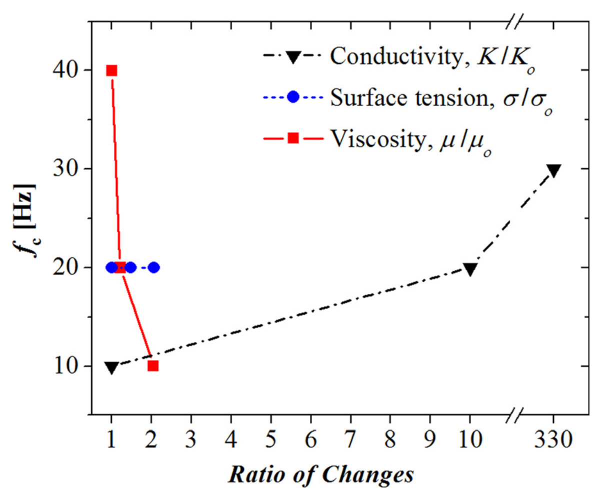

FIG. 4. Correlation between f_c and ratio of change ($K_o = 50\,\mu$S/cm, $\sigma_o = 31$ mN/m, and $\mu_o = 2.73$ mPa s).

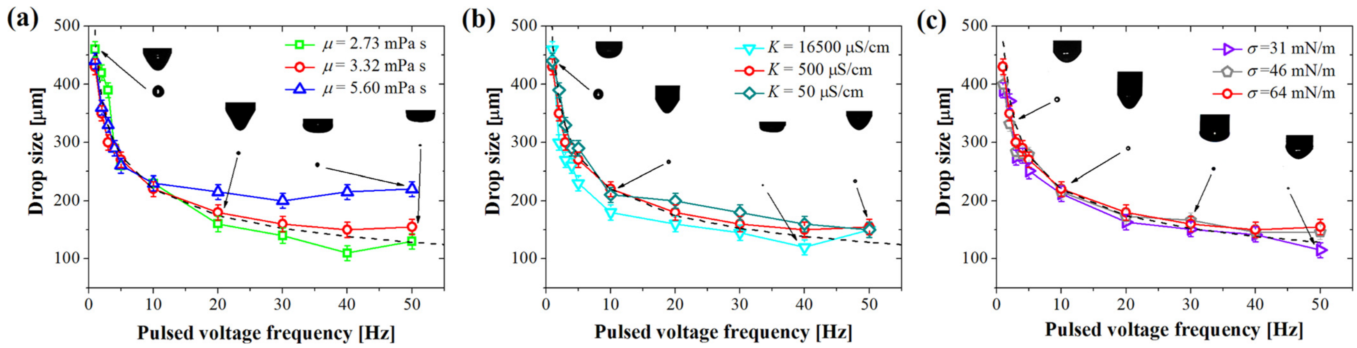

FIG. 5. Correlation between voltage frequency and drop size: (a) effect of viscosity for fixed $K = 500\,\mu$S/cm, $\sigma = 64$ mN/m, (b) effect of electrical conductivity for fixed $\mu = 3.32$ mPa s, $\sigma = 64$ mN/m, (c) effect of surface tension for fixed $K = 500\,\mu$S/cm, $\mu = 3.32$ mPa s (Dashed curve: calculated drop size based on mass conservation.)

and not a function of σ. Note that the duration (τ) is in the range of several ms. If $\tau = 2$ ms, then the maximum allowable voltage pulse is 500 Hz. Our experiments do not support the applicability of Eqs. (1) and (2) for voltage frequencies exceeding 50 Hz. It appears impossible to have a printing frequency greater than about 100 Hz in practice. We confirmed this assessment with actual printing frequencies from several preceding studies.[17–19]

To better understand why the fulcrum frequency is so much less than the theoretical maxima predicted through relaxation times, an additional analysis was sought. A Taylor cone forms in the presence of an electric field at the nozzle tip. The electric field[20] and characteristic time[21] for Taylor cone formation are

$$E_{tip} = \frac{2V}{r\ln\left(\frac{4L}{r}\right)} = 7.60 \times 10^6\,\mathrm{V/m}, \tag{3}$$

$$T = 3^{3/2}\sqrt{\frac{\rho}{\varepsilon_o^3}}\left(\frac{\pi\sigma}{E_{tip}^3}\right) = 2.99\,\mathrm{ms}. \tag{4}$$

This theoretical maximum fulcrum frequency, $f_c = 1/2T = 167$ Hz, is more than four times the measured fulcrum frequency.[22]

Note the absence of μ and K in Eqs. (3) and (4). This indicates that the actual DOD performance, in addition to being dependent upon the electrical conductivity and viscosity, is also dependent upon liquid density, surface tension, and applied voltage, along with nozzle radius and nozzle-to-substrate distance. To better characterize the performance of DOD as a function of electrical conductivity and viscosity, a dimensionless parameter has been introduced[23]

$$\delta_m = \sqrt[3]{\frac{\rho\varepsilon_o\sigma^2}{K\mu^3}} \tag{5}$$

Control of drop size is another important process in inkjet printing. Figure 5 shows how drop size varies as a function of pulsed voltage frequency when changing liquid properties. Drop size is related to the number of drops formed because volume flow rate = single drop volume × drop generation frequency. From conservation of mass, the expected drop size for perfect DOD is represented with the black dashed curve. The overall drop size tends to decrease with decreasing in viscosity and increasing in electrical conductivity. Surface tension does not exert significant control on drop size; variation is within experimental uncertainty.

Measured drop sizes are often bigger than the expected size (in Figure 5) with observations exceeding the perfect DOD line. Beyond 50 Hz in Figure 3, the drop-generation frequency decreases for all cases and the drop-formation rate becomes non-uniform and deviates from the DOD line. In addition to a non-uniform drop generation rate, the drops are larger. Both of these characteristics degrade print quality.

To better characterize the performance of EHD inkjet printing (specifically f_c), a dimensionless universal coefficient is formed that contains the three liquid properties varied in these experiments:

$$C_u = Re^{10} \times We \times N_e \times \frac{\tau_f}{\tau_e{}^{0.1}} = \frac{(\rho u D)^{11}}{2}\left(\frac{V}{\sigma}\right)^2\frac{K^{0.1}\varepsilon^{0.9}}{\mu^{10}} \tag{6}$$

where Re is the Reynolds number, We is the Weber number, and N_e is the dimensionless charge level. To emphasize the known important effect of viscosity, Re is raised to the power of 10, while τ_e is raised to the power of -0.1 to de-emphasize the effects of electrical conductivity. As shown in Figure 6, f_c is a linear function of C_u and this empirical formula is appropriate for the proposed range of f_c and C_u.[24]

These experiments demonstrate improved DOD performance with decreased viscosity and surface tension, and increased electrical conductivity. However, if the viscosity

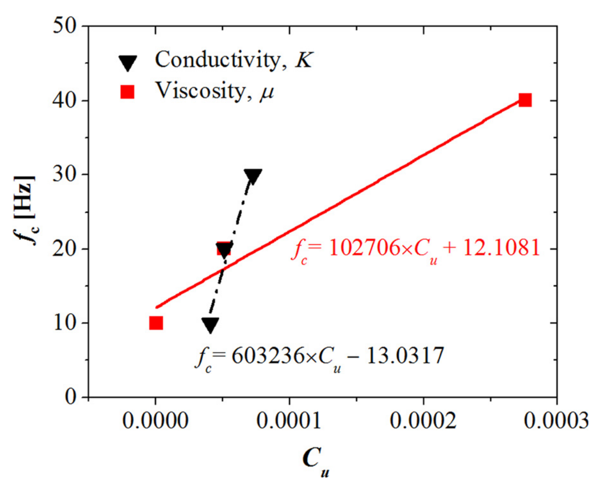

FIG. 6. Correlation between f_c and C_u.

and surface tension are too low or electrical conductivity is too high, drop generation may become unstable. DOD performance requires small drops and a uniform drop-formation frequency. Experiments show limits of less than 50 Hz for perfect DOD performance, which are far less than the hydrodynamic and charge relaxation times and Taylor cone formation time suggest. Clearly, liquid properties should be carefully considered when optimizing EHD inkjet printing. The effects of each parameter need to be characterized to establish the expected quality of inkjet printing, and for the range of fluid properties considered here, a dimensionless universal coefficient has been proposed.

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