A New AC Electrospray Mechanism by Maxwell-Wagner Polarization and Capillary Resonance

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We report a new high-frequency (> 10 kHz) AC electrospray that is capable of generating micron-sized electroneutral drops. Unlike its DC counterpart, the drops are not ejected continuously from a sharp Taylor cone but intermittently from a resonating meniscus at the orifice. We attribute the resonant frequency to the capillary-inertia vibration time of the meniscus and the drop ejection to the Maxwell-Wagner electric stress at the drop tip, which is observed to reverse its direction across a crossover frequency. Above this frequency, the oppositely directed Maxwell-Wagner force causes the liquid to recede up the micro-needle as an apparent electrowetting effect.

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Electrospraying is commonly used for the production of fine mono- and poly-dispersed drops in widespread applications such as electrospray ionization mass spectrometry for protein and DNA characterization [1], respiratory drug delivery [2], microencapsulation, etc. Electrospraying, in general, employs the principle in which the applied electrical stress stretches the liquid meniscus at the capillary tip which subsequently deforms and breaks off. With the exception of a few recent studies, the major work has focused on DC fields [3]; the few AC studies available have been limited to either DC superimposed AC fields [4] or low AC frequencies [5]. In this communication, we report a new electrospray phenomenon in which micron-sized ethanol drops are generated at high AC frequencies (10–280 kHz). The spray modes observed, as well as the electroneutrality and dimensions of the drops produced, are distinct to that in DC electrospraying, thus extending the use of electrosprays to a wider area of possible application. We shall proceed by describing the experimental setup and observations, followed by an attempt to elucidate the various complex spray phenomena observed by employing simple scaling arguments.

The experimental apparatus is schematically described in Fig. 1. A metal hub micro-needle (Hamilton N733) with nominal O.D. 0.21 mm and thickness 0.05 mm, mounted at 50° to the horizontal, is connected to a high voltage output transformer (Industrial Test Equipment) and RF amplifier (Powertron 250 A 10 Hz–1 MHz), capable of delivering up to 6000 V (peak-to-peak) and 250 W; AC frequencies were produced by a function/arbitrary waveform generator (Hewlett-Packard 33120A). The ground electrode consisted of a strip of copper tape placed 5 mm away from the needle tip. Spray development was imaged using a high speed video camera (Kodak Ektapro 1000 Imager and High-Spec Processor) at record rates of 1000–6000 frames/s, connected to a telescopic lens to achieve an overall magnification of 800x; background illumination was provided by a fibre-optic lamp (Fiber-Lite PL-800). The working liquid is 95% ethanol (AAPER Alcohol & Chemical Co. 190 Proof), with interfacial tension $\sigma \sim 25$ mN/m, density $\rho \sim 816$ kg/m$^3$, viscosity $\mu \sim 1.2$ mPa.s, conductivity $\kappa \sim 4 \times 10^{-5}$ S/m, and, relative permittivity $\varepsilon_r = 24.3$.

Fig. 2 depicts the delineation between the various spray regimes observed as a function of both the applied frequency, $f$, and the applied peak-to-peak voltage, $V$. In all cases, the flight of the ejected micron-sized drops do not follow the field lines; the drops can also be easily deflected by cross flow. In addition, the current arising from the charge carried by the drops was undetectable due to the presence of background AC current. Thus, unlike DC electrosprays, the drops are believed to be electroneutral. Perhaps the most fundamental observation of the high frequency AC electrospray modes in our experiments is the absence of a well-defined Taylor cone (formation of a conical meniscus with a half angle close to the Taylor angle of 49.3°), which is primarily characteristic of the predominant stable cone-jet mode in DC electrosprays [3]. In addition, none of the other DC electrospray modes such as dripping, intermittent cone-jet, ramified jet or spindle modes [3] are observed. Instead,
the meniscus is seen to resonate at some characteristic frequency, \( f_1 \sim 10 \) Hz, periodically ejecting drops with diameters estimated to be of order 10 \( \mu \text{m} \), either at the same characteristic frequency or at another distinct characteristic frequency, \( f_2 \sim 10^3 \text{ Hz} \). However, drop ejection is limited to a voltage window, which is a function of \( f \). Below this window, there is insufficient electrical force to overcome the capillary force at the tip of the meniscus. Above the window, wetting is observed to draw liquid up the needle. The low frequency ejection mode resembles drop pinch-off due to wetting effects, tip streaming \[6\] from a transient cone or a microjet that forms intermittently from the resonating meniscus at frequency \( f_1 \). 

The high frequency mode involves the ejection of single or multiple drops at the end of the tip or microjet at frequency \( f_2 \). The multiple spray modes and the bi-periodic behaviour observed thus indicate the influence of several competing and interacting physical effects on the drop.

A candidate for the driving electric force is the AC Maxwell stress due to field-induced double layer polarization at the interface \[7\]. From the liquid conductivity, an ionic concentration, \( c \), of roughly \( 10^{-7} \) M is obtained, from which we deduce the double layer thickness, \( \lambda = \left[\frac{\varepsilon_\text{f} R_\text{g} T_\text{f}}{2F^2z^2c}\right]^{1/2} \), to be approximately 0.2 \( \mu \text{m} \); \( \varepsilon_\text{f} \) being the liquid permittivity \( (\varepsilon_\text{f} = \varepsilon_\text{r} \varepsilon_\text{a} \text{ where } \varepsilon_\text{r} \text{ is the vacuum permittivity}) \), \( R_\text{g} \) the molar gas constant, \( T_\text{f} \) the absolute temperature, \( F \) the Faraday constant and \( z \) the ionic valency. This relatively thick double layer translates into a Debye diffusion time, \( T_\text{d} \sim \lambda^2/D \), of \( 10^{-3} \) s, \( D \) being the ionic diffusivity, which is larger than the period of the applied AC field, \( T \). Moreover, if AC charging of the double layer were to be the responsible mechanism for the polarization, the spray regimes observed would be very sensitive to the double layer thickness and hence the ionic concentration. Nevertheless, the use of ethanol with lower ionic concentrations as well as the addition of 1 ppm hydrochloric acid (HCl) to increase the ionic concentration, so that the conductivities varied between 10 to 100 times in either direction, did not yield significant quantitative or qualitative difference in the results. This is due to the large time scale for bulk ionic diffusion, \( R^2/D \), of \( 10^3-10^4 \) s, where \( R \) is the apparent length scale of the drop taken to be 5 mm (approximated by factoring the drop curvature at the needle tip by 10 to account for the entire drop radius), compared to \( T \).

A comparison of the drop viscous drainage times due to Maxwell-Wagner and double layer interfacial polarization, \( T_{MW} \) and \( T_{DL} \), respectively, obtained via a balance of the relevant force \( (F_{MW} \sim \Re[\varepsilon CM\varepsilon a E_\infty]^2 \text{ and } F_{DL} \sim Q\varepsilon_\infty R^2z^2; \varepsilon_\infty \sim V/L \text{ is the applied field and } L \sim 5 \text{ mm is the electrode separation}) \) with viscous dissipation \( \mu L/R \) (see Table I), yields \( T_{DL}/T_{MW} \sim \Re[\varepsilon CM]\varepsilon a R^2z^2Q^{-1}L^{-1} \sim 10^8 \). Here, \( U \) is the characteristic velocity and \( Q \) is the charge \( (Q = cN_\text{Ae}R^3, \text{where } N_\text{A} \text{ is Avogadro’s constant and } e \text{ is the electronic charge}) \). \( f_{CM} \) is the Maxwell-Wagner form of the Clausius-Mossotti polarization factor that allows for a reactive current:

\[
f_{CM} = \frac{\tilde{\varepsilon}_0 - \tilde{\varepsilon}_r}{\tilde{\varepsilon}_r + 2\tilde{\varepsilon}_a}.
\]

\( \tilde{\varepsilon} \) indicates a complex permittivity given by \( \tilde{\varepsilon} = \varepsilon - i(\kappa/\omega) \), where \( i = \sqrt{-1}; \text{ the subscripts } l \text{ and } o \text{ referring to the liquid and the ambient medium, respectively. The conductivity } \kappa \text{ accounts for ion motion across the interface due to a gas-phase or interfacial liquid ionization reaction to be described subsequently. } f_{CM} \text{ thus represents the dependence of the effective polarizability of the liquid on the angular frequency of the applied field } \omega (= 2\pi f) \). Since \( T_{DL} \gg T_{MW} \), and as \( T_{MW} \sim T \), it is Maxwell-Wagner interfacial polarization that is responsible for the generation of the dipole moment at the meniscus tip. Furthermore, the ratio of the instantaneous induced surface charge due to Maxwell-Wagner polarization, \( \varepsilon_0f_{CM}E_\infty \), to that due to AC double layer charging in one half cycle, \( \kappa_1TE_\infty \), is approximately \( T_d/T \) since \( T_d \sim \varepsilon_0/\kappa_1 \). For ethanol, \( T_d/T \sim 10^3-10^4 \), thus suggesting that double layer charging in the case of weak electrolytes is negligible. It can be seen that when \( f \lesssim 10 \) Hz, \( T_d \lesssim T \) and hence double layer charging then becomes significant. An important consequence of this is that, in the absence of significant gas or interfacial liquid ionization, the drops produced by this mechanism are electroneutral, consistent with our observations, since the meniscus polarization is due to transient molecular dipoles at the tip that relaxes rapidly in the ejected drop. This is in contrast to double layer polarization in DC electrospays of electrolytes which produces drops with a permanent charge. Further support for the Maxwell-Wagner
The wetting phenomena can be explained by consideration of the Maxwell-Wagner polarization mechanism, embodied by Eq. 1. Fig. 4 illustrates the magnitude of the real and imaginary parts of $f_{CM}$ as a function of $f$. We note the existence of a crossover frequency, $f_c$,

$$f_c = \frac{1}{2\pi} \sqrt{\frac{(\kappa_0 - \kappa_i)(2\kappa_0 + \kappa_i)}{(\epsilon_0 - \epsilon_i)(2\epsilon_0 + \epsilon_i)}},$$

where the sign of Re[$f_{CM}$] reverses. If the electric field is oriented towards the needle tip, molecular polarization bestows a net positive charge at the surface as illustrated in Fig. 4. Nevertheless, despite the change in the orientation of the electric field in every half AC cycle, the Maxwell stress remains oriented in the direction of the needle tip thus flattening the drop around the orifice and causing liquid to recede up the needle as an apparent electrowetting effect, which, in turn, suppresses drop pinch-off. This was confirmed by experiments with a low conductivity fluid such as toluene $[\kappa < 10^{-12} \text{S/m}; \; f_c \sim 5 \text{ kHz}]$, which resulted in severe wetting where drop pinch-off was completely suppressed. However, this effect is only observed at frequencies above $f_c \sim 30 \text{ kHz}$ when there is insufficient time for interfacial ionization reaction to occur. Below $f_c$, interfacial reaction charging is dominant therefore producing an excess of negative ions at the interface. This results in an oppositely directed force which acts to stretch the drop, thus giving rise to tip streaming and microjet ejection.

Both the dependence of the onset voltage on $f$ in Fig. 2 as well as the onset of wetting to produce the drop pinch-off mechanism are consistent with the Maxwell-Wagner polarization mechanism. In this mechanism, the drop can be represented by a simple parallel resistor-capacitor circuit; the build up of charges due to the interfacial ionization reaction acts like a dielectric capacitor of capacitance $C$ whereas the ionization reaction can be represented by a Faradaic reaction resistor of resistance $R$. A larger potential drop across the capacitor at low $f$ results in positive polarization whereas insufficient time for the reaction to occur leads to a larger potential drop across the resistor at high $f$. The latter results in negative polarization and hence wetting. The Maxwell stress, $\tau_m$, thus reverses direction at $f_c$; we note that $f_c$ in Eq. 2 is associated with the relaxation time of the polarization as the applied field reverses, i.e. $f_c \sim 1/\tau_c$. From our measurements, we estimate $R \sim 2 \text{ M}\Omega$ and $C \sim 10 \text{ pF}$, corresponding to a $\tau_c$ relaxation frequency, $f_{RC} \sim 1/\tau_c$, of the relevant time scale $[9]$. Careful examination of Fig. 3 indicates that the microjet ejection mode is a transition between the tip streaming and wetting modes: As $f$ increases, the number of drops ejected from the microjet decreases therefore approaching a single periodic ejection with frequency $f_1$, i.e. $f_2 \rightarrow f_1$.

The wetting modes, on the other hand, are monoperiodic, where drop pinch-off occurs at frequency $f_1$. The wetting phenomena can be explained by consideration of the Maxwell-Wagner polarization mechanism, embodied by Eq. 1. Fig. 4 illustrates the magnitude of the real and imaginary parts of $f_{CM}$ as a function of $f$. We note the existence of a crossover frequency, $f_c$,

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\[ f_c = \frac{1}{2\pi} \sqrt{\frac{(\kappa_0 - \kappa_i)(2\kappa_0 + \kappa_i)}{(\epsilon_0 - \epsilon_i)(2\epsilon_0 + \epsilon_i)}}, \]
TABLE I: Typical length/time magnitudes for the relevant physical effects governing the dynamics of drop ejection.

<table>
<thead>
<tr>
<th>Physical effect</th>
<th>Scaling</th>
<th>Magnitude</th>
</tr>
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<tbody>
<tr>
<td>Viscous drainage time due to double layer polarization</td>
<td>$T_{DL} \sim \mu R^2 L Q^{-1} V^{-1}$</td>
<td>$10^{-4}-10^{-5}$ s</td>
</tr>
<tr>
<td>Viscous drainage time due to Maxwell-Wagner polarization</td>
<td>$T_{MW} \sim \mu L^2 \text{Re}[f CM]^{-1} \epsilon_0^{-1} V^{-2}$</td>
<td>$10^{-6}$ s</td>
</tr>
<tr>
<td>Maxwell-Wagner polarization-capillary force balance</td>
<td>$V_c \sim (\sigma L^2 f CM \epsilon_0^{-1} R^{-1})^{2/3}$</td>
<td>$10^3$ V</td>
</tr>
<tr>
<td>Viscous-capillary pinch-off time</td>
<td>$\tau_c \sim \mu R \sigma^{-1}$</td>
<td>2x10^{-5}-5x10^{-5}$ (jet)</td>
</tr>
<tr>
<td>Capillary-inertia pinch-off time</td>
<td>$\tau_i \sim (\rho R^2 \sigma^{-1})^{1/2}$</td>
<td>$10^{-3}$ s (jet); $10^{-1}-10^{-2}$ s (drop)</td>
</tr>
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which corresponds to a frequency, $f_p$, of order 100 kHz. Thus, $f_p$ which lies between $f_c$ and $f_{RC}$, provides an estimate at which the onset of wetting at $f_c$ completely suppresses the tip streaming and microjet ejections, i.e., where $f_2 \rightarrow f_1$. Despite having allowed for the liquid and air conductivity in our estimation of $T_p$, it is believed that the associated AC current is not carried by the ions within the ethanol drop but rather by the ions produced by atmospheric or interfacial liquid ionization at the meniscus tip. At very high voltages ($V \gg 6000$ V), corona discharge is observed, causing meniscus elongation and drop ejection to cease, therefore further supporting the postulation that the polarization at the tip involves a current. Although this current produces a net charge at the tip in every half cycle of the applied field, the long drop ejection time scale ($10^{-3}$ s) corresponding to $f_1$ compared to the period of the applied field stipulates that the ejected drop will remain electroneutral.

around 200 kHz, consistent with the observation of complete wetting at $V_c$. Nevertheless, wetting also occurs at frequencies other than $f_{RC}$ and at voltages beyond $V_c$. This may be due to threshold voltages for ionization or for electrowetting. Nevertheless, it is quite reasonable that the Maxwell-Wagner electric Maxwell stresses, both towards the tip which causes drop ejection, and in the opposing direction which causes wetting, reach a maximum when $f \sim f_{RC}$. When $f \ll 1/\text{RC}$, there is maximum meniscus polarization $p$ at the tip due to the excessive ions produced by the interfacial reaction that also screens the normal field $E_n$. Since $\tau_n = p E_n$, $\tau_n$ is expected to decrease as $f$ decreases. When $f \gg 1/\text{RC}$, there is considerably less polarization and screening that again leads to a decrease in $\tau_n$. The optimum frequency, $f_{RC}$, where $\tau_n$ is maximum, therefore explains the minimum on the onset voltage at 180 kHz in Fig. 2.

Both $f_c$ and $f_{RC}$ can also be related to the Maxwell-Wagner polarization time, $T_p$, given by

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