The transport of aerosol micro-droplets through an atmospheric pressure plasma:

Paul Maguire
Plasmas and Nanofabrication
University of Ulster

P Maguire\textsuperscript{1} C. Mahony\textsuperscript{1}, N Hamilton\textsuperscript{1}, C Kelsey\textsuperscript{1}, E Bennet\textsuperscript{2}, D Rutherford\textsuperscript{1}, DA McDowell\textsuperscript{1}, H Potts\textsuperscript{2}, D Diver\textsuperscript{2}, D Mariotti\textsuperscript{1}

1. Engineering Research Institute, University of Ulster, Belfast BT37 0QB
2. SUPA, School of Physics and Astronomy, University of Glasgow, Glasgow
Low-temperature atmospheric pressure plasmas

- Non-equilibrium atmospheric pressure plasmas
- Low-temperature (gas 300-1000 K; $T_e > 1$ eV)
- Micro-/millimeter scale confinement (0.25-2 mm diameter)
- RF (13.56 MHz) with DC-pulse ignition/triggering
- Various configurations ...
- ... “two-ring” configuration:

From inorganic, droplets to bacteria

Gas precursors (or solid/liquid) → Nanoparticles

Aerosol → Droplets ...

Aerosol With bacteria → ... charged bacteria

inert gas background (e.g. He, Ar, Ne etc.)
A complicated scenario for droplets

- As seen before, electron/ion currents contribute to particle heating and this is still applicable to liquid droplets (water/ethanol mixtures here).

- **HEATING** induces droplet evaporation so that these are expected to reduce in size as they travel through the plasma.

- **CHARGING.** The high electron mobility does induce a net charge on the droplet which can reduce the droplet size by electrostatic repulsion at the Rayleigh limit.

- **CHEMISTRY.** Finally, the electron current also induces a form of “electrochemistry”, inducing reactions within the droplets; it is important to underline that this is different from gas-phase plasma chemistry.
Challenges

2.0 mm ID PLASMA SOURCE
Visualization

AEROSOL + PLASMA ON
Droplet size and speed

Aerosol Characteristics
Experimental: imaging set-up

- iStar Camera
- Spacers and Swivel Coupler
- Questar Microscope
- Plasma/Aerosol Source
- Quartz Tube Exit
- Field of View
- 1500 \( \mu \text{m} \)
- 1872 \( \mu \text{m} \)
- Depth of Field \(~ 150 \mu \text{m}~\)
Droplet imaging

Plasma OFF
Gas velocity (average) 16 m/s
Distance from tube 4 mm
Exp time 20 µs
500 Images

Droplet
Diameter = 40 µm
Velocity = 26 m/s

Estimated $10^5$ droplets per second
Velocity

- **Gas flow**
  - Low Reynolds No
  - Expected to be laminar
  - Parabolic velocity profile

- **Droplet**
  - Normalised to average gas velocity
  - Parabolic velocity envelope
  - Little variation with plasma

![Graph showing normalized velocity](image)

1.5 mm, $V_{gas}: 32 \text{ m/s}$
Velocity

• Gas flow
  - Low Reynolds No
  - Expected to be laminar
  - Parabolic velocity profile

• Droplet
  - Normalised to average gas velocity
  - Parabolic velocity envelope
  - Little variation with plasma

Droplet velocity normalised to expected radial gas velocity

• 0.8 typical
• <0.3 near wall
• Approaching turbulence for mixed phase flow

1.5 mm, $V_{\text{gas}}=32$ m/s

Quartz Wall
Time-varying electric field on droplet

Oscillating plasma and electric fields
13.56 MHz, 70ns period

Plasma region
*quasi-neutral* $E=0$

Field region, $E<0$
*net positive charge*

Time-averaged
*Droplet time of flight*
40us – 100us
*i.e. >1000 rf periods*

Electric field tends to nudge
negatively charged droplet
towards centre of channel,
away from walls
Droplet Diameter

- Log Normal distribution
  - commonly used to describe aerosol characteristics
Droplet Diameter

- Log Normal distribution.
- Typical nebuliser characteristics, unconstrained

Probit: inverse standard normal distribution function

Count mean diameter falls from 15 μm to 13 μm with plasma exposure.

Evaporation for 2-phase system

\[ D^2 = D_0^2 - ct \]

\[ c \sim 10^{-7} \text{ m}^2\text{s}^{-1}. \]
Evaporation

- Evaporation: \( D^2 = D_0^2 - ct \)
- \( c \) (plasma ON) = \( 2 - 5 \times 10^{-7} \) m\(^2\)s\(^{-1}\).

Heinisch et al.
- Evaporation rates for water - measured by Raman in ED trap at 25°C
  - \( c = 1.5 \times 10^{-10} \) m\(^2\)s\(^{-1}\) humid, still N\(_2\)
  - \( c = 1.5 \times 10^{-9} \) m\(^2\)s\(^{-1}\) for dry flowing N\(_2\)
  - x 100 lower

Benson et al.
- Simulation ICP plasma with Argon gas temperature of 3000 K
  - (365 K Wet Bulb Temp)
  - \( c = 5 \times 10^{-7} \) m\(^2\)s\(^{-1}\)

- Mass reduction cannot be explained by simple evaporation alone

- Additional effects must be present.
  - Ion neutralisation on H\(_2\)O surface (24eV)?
  - Ion interaction with H\(_2\)O vapour layer?

Gas temperature
OES: Comparison of Aerosol and Dry Plasma

Experimental setup: optical fibre collecting light from the area between the two plasma electrodes

Typical Dry Plasma

Dry Plasma:
He Flow – 3.5 sdm
Ne Flow – 0.5 sdm

Typical Plasma with aerosol

Aerosol Plasma:
H₂O Flow – 0.6 ml/hour
He Flow – 3.5 sdm
Ne Flow – 0.5 sdm

Broadband spectrometer: it is clear that the OH drops relative to both Nitrogen and to Ne lines.

Spectrometers
UV : 299.3 → 397.1 nm
BRB : 194 → 1122 nm

Data sets taken:
1.) BRB – quick overview to look for differences in the spectra dry vs. with aerosol
2.) Dry Plasma, UV spectrometer, 5s integration time, 100 sequential shots (no BG)
3.) Dry Plasma, UV spectrometer, 30s integration time, 100 sequential spectra
4.) Aerosol Plasma, UV spectrometer, 30s integration time, 100 sequential spectra
OES spectra 300 – 400nm: with and without aerosol

Electronic quenching of OH(A) by water in atmospheric pressure plasmas and its influence on the gas temperature determination by OH(A–X) emission

Peter Bruggeman¹,², Felipe Iza³, Peter Guns³, Daniel Lauwers³, Michael G Kong³, Yolanda Aranda Gonzalvo³, Christophe Leys² and Daan C Schram¹
Temperature Fits

Temperature Fit Ranges:
280 – 350 K without aerosol
330 – 400 K with aerosol

Best fits at around 330 K

0-2 N₂ Band
Dry Plasma gas temperature

Each point is a obtained by fitting synthetic spectra to an individual spectrum.

**OH** fits from data set 2 yielded average **OH** rotational temperatures of 328 K.

Average **OH** temperature = 328 K.

Average **N₂** temperature = 327 K.
Both temperatures hotter now, but steady with time, OH temp consistently higher than the N$_2$ temp. This is due to the higher water vapour content – error in determining T from OH.

*Each point is a obtained by fitting synthetic spectra to an individual spectrum*
Plasma Theory - Droplet Charge
Plasma Charging, collisionless

Droplet enters plasma discharge

Surface bombarded by electrons and ions

Surface charges negatively

Sheath forms between surface and plasma

Incoming/outgoing ion/electron currents balance

Droplet reaches plasma potential $\Phi$

Dynamic equilibrium established

Droplet charge $Q$ depends on plasma parameters

$Q_0 = \Phi \epsilon_0 4\pi r_0 e^{r_0/\lambda_D}$

$$\Phi \approx -0.73T_e \ln \left( \frac{m_i T_i n_i^2}{m_e T_e n_e^2} \right)^{1/2}$$

Simulating charge and evaporation dynamics
Euan Bennet, Hugh Potts, Declan Diver
Plasma charging, collisional model

• Parameters of interest
  ➔ Initial charging rate
  ➔ Steady-state charge & floating potential
  ➔ Sheath & afterglow neutralisation

• Highly collisional
  ➔ Hydrodynamic solution
  ➔ No analytical approximations
  ➔ Simulations
  ➔ Asymptotic analytical approximations
  ➔ Not experimentally verified

\[
\nabla \left( -\frac{\partial n_i}{\partial r} - \frac{1}{\tau} n_i \frac{\partial \phi}{\partial r} \right) = 0
\]
\[
\nabla \left( -\frac{\partial n_e}{\partial r} + n_e \frac{\partial \phi}{\partial r} \right) = 0
\]
\[
\nabla \left( \frac{\partial \phi}{\partial r} \right) - \frac{1}{\lambda_D^2} (n_e - n_i) = 0
\]
\[
\nabla (x) = 1/r^2 \partial / \partial r (r^2 x)
\]
\[
\Gamma_i^p = \frac{N_\infty D_i}{R_p} \frac{\partial n_i}{\partial r} (r_p)
\]
\[
\Gamma_e^p = (N_\infty D_e / R_p) \partial n_e / \partial r (r_p)
\]

• Electron density
  \[1 \times 10^{12} - 1 \times 10^{14} \text{ cm}^3\).
  \[\text{Average R: } Q_d = 10^4 e - 10^5 e\]
  \[\text{Max. R: } Q_d = 10^5 e - 10^6 e\]
Charge density estimation

- Measurements of Plasma Current, Voltage & Phase with Impedans OCTIV IV probe
  - RF power 60 W
  - $Q_{\text{Ne}}$ 0.7 slm
  - $Q_{\text{He}}$ 1.0 slm
  - $Q_{\text{liquid}}$ 0.3 ml/hour

- Three Plasma Conditions:
  - Gas
  - Gas & liquid ($Q_{\text{liquid}} = 0.3$ ml/hour)
  - Gas & liquid ($Q_{\text{liquid}} = 0.3$ ml/hour) & pollen grains (~ $10^4$/ml)

- Time Averaged Sheath Width
  - Gas ~ 105 $\mu$m
  - Gas & liquid ~ 200 $\mu$m
  - Gas, liquid & pollen ~ 200 $\mu$m

- Time Averaged Electron Density
  - Gas ~ $3 \times 10^{12}$ cm$^{-3}$
  - Gas & liquid ~ $7 \times 10^{12}$ cm$^{-3}$
  - Gas, liquid & pollen ~ $3 \times 10^{12}$ cm$^{-3}$

30 micron diameter lycopodium grains
Rayleigh limit

\[ Q_R = 8\pi \sqrt{\varepsilon_0 \gamma r_d^3} \]

\( \gamma \) is the surface tension of the liquid

• Equivalent \( R_{\text{rayleigh}} \)

• \( Q_d/Q_r \): maximum is \(~5\%\)
Droplet Charge Measurement
Charge measurement

• Charge amplifier
  ※ High feedback impedance
  ※ Current feedback amplifier: Amptek A250
  ※ Max sensitivity: 0.16 µV/electron
  ※ Gain determined by both collector & amplifier

• Rise time
  ※ Droplet approach to collector
  ※ Electrostatic models
  ※ Physical calibration
  ※ Provides estimate of system gain

• Fall time
  ※ Circuit response, shape amp
Measurement calibration

- **Extended Shielded Enclosure**
  - Reduces 50Hz noise
  - Gives velocity ~ 4 m/s

- **Ring Collector**
  - 4mm ID, 32 mm OD
  - fall ~ 0.7 m
  - vel ~ 3.8 m/s

- **Plain Collector at base**
  - 32 mm OD
  - fall ~ 0.87 m
  - vel ~ 4.2 m/s

**2mm DIAMETER DROPLETS**
- 0.63 mm syringe needle
- syringe pump
- Biased up to 150 V
- Droplet diameter ~ 2 mm
- Droplet frequency ~ 0.5 to 2 Hz
Good s/n with A250 & A250 F amplifiers

Ring Collector
- signal rises as droplet approaches
- quickly reverses at collector centre
- decays as droplet leaves
- no minor peak
- drop - plain collector effect seen

Plain collector
- signal rises as droplet approaches
- minor peak at impact
- Minor peak is thus due to impact
- Majority of charge transfer is due to electrostatic induction
Comsol model – induced charge, ring
Comsol: Ring collector

Plate 30 mm
Ring 4 mm
Drop 2 mm
Q \approx 1.7 \times 10^{-11} \text{ C}
\approx 10^8 \text{ electrons}
V 150 V
Induced current model, plate

Droplet approach
- at distance $x$,
- collector diameter $D$

\[ i_n = \frac{q_n v_n D^2}{2\pi (D^2 + x_n^2)^{3/2}} \]
Calibration factors

**CHARGE AUDIT**
Charge used in 2mm droplet models
1.1 x 10^8 electrons
~1.8 x 10^{-11} Coulomb
~ 150 V

Charge collected
1.0 ± 0.1 x 10^8 electrons

**AMPLIFIER GAINS**
A250 x -300 ± 20
A250F x -1000 ± 50
Plasma/aerosol charge measurement

No Aerosol

Amp: A250F
Scope: 1MOhm
Pf RF: 110W W
Ne: 1slm
He: 3.5 slm
Q_{H20} 0 ml/hr

NOISE WITH NEBULISER OFF
Plasma/aerosol charge measurement

**With Aerosol**

- **Amp:** A250F
- **Scope:** 1MOhm
- **Pf RF:** 110W W
- **Ne:** 1slm
- **He:** 3.5 slm
- **Q\textsubscript{H2O}** 0.03 ml/hr

**Q \sim 3 \text{ to } 9 \times 10^7 e**

Charge resolution limit

\sim 1.5 \times 10^7 e
Plasma/aerosol charge measurement

With Aerosol
Amp: A250F
Scope: 1MOhm
Pf RF: 110W W
Ne: 1slm
He: 3.5 slm
Q_{H2O} 0.03 ml/hr

Q \sim 3 \text{ to } 9 \times 10^7 \text{ e}

- Charge resolution limit
  \sim 1.5 \times 10^7 \text{ e}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Plasma_and_Aerosol_Droplet_Distribution.png}
\caption{Droplet Diameter Distribution}
\end{figure}

\textbf{Droplet Dimensions:} 13\,\mu m \text{ median}
\textbf{Frequency:} \sim 10^5 /\text{second}
\textbf{Charge:} \sim 10^5 \text{ electrons}

\textbf{Un-amplified data}
\textbf{DC voltage shift of} \sim -0.53 \text{ mV}
- commensurate with
[\sim 10^5 \text{ droplets/second}] \ast \left[ \text{with } \sim 10^5 \text{ electrons each} \right]
\sim 10 \text{ - 20 micron diameter}
Single droplet on demand
Single Droplets

Pressure Controller  Voltage and Strobe Controller

MJ-ATP-01
20 µm & 70 µm Dispensing Devices

Outer electrode (grounded)
Piezoelectric
Inner electrode (voltage pulse)

Meniscus kept level by controlling reservoir head pressure
Plasma

- 150 sccm helium
- 100 W power (<1W reflected)
- No Neon or other gas flow
Single droplet into plasma

**Water Jet**
- 100 Hz repetition rate
- Settings gave droplet velocity of 2 ms\(^{-1}\) in previous measurements

**Imaging**
- Integration time of 0.079ms per frame
- This implies that each image/frame is an accumulation of 8 consecutive droplets at equal strobe delay
- Plasma imaging is continuous
Single Droplets

Graph showing the relationship between Diam (micron) and Vel (m/s).

Graph illustrating various droplet diameters and initial droplet velocities.

Graph depicting stopping distance against initial droplet velocity with different droplet sizes and cutoff angles.

www.nibec.ulster.ac.uk/maguire
Plasma Interaction with Individual Planktonic Bacteria
Aerosol droplet size control

If droplet size can be controlled to contain only one bacterium, then effects on individual bacteria can be studied rather than agglomerates. Size ranges around 5 micron. However, aerosol generation gives large droplets or very small (< 1um). Also, the evaporation rate will be much greater.

Effect of charge transfer onto single bacterium and subsequent transport on surface then physical impact on structure to be determined from physical and microbiological experiments.

Full evaporation. Single charged bacteria in either dessicated or hydrated state. Amount of charge transferred to microbes or leaves with water vapour unknown.
Apparatus
Aerosol Collection

- Apparatus: Modified gas washing bottle
  - 100 ml Schott bottle; tubing 10cm, Air-tight ‘closed’ system
- Aerosol impingement directly into liquid (5ml)
- Type of collection liquid different depending on the measurement

<table>
<thead>
<tr>
<th>Liquid Type</th>
<th>Measurement</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nutrient Broth</td>
<td>Growth (Viability)</td>
<td>Agar Plate Colony Count &amp; Optical Density @ 600 nm</td>
</tr>
<tr>
<td>Tris-HCl / EDTA (TE) Buffer</td>
<td>Released (Free) DNA</td>
<td>Concentration (A_{260} / A_{280})</td>
</tr>
</tbody>
</table>

- Nutrient Agar (universal)
- Chromocult (coliform only)
Experimental Details

- Bacteria: *E. coli (K-12)* mid-exponential growth phase; diluted to $10^5$ cfu/ml in Ringer’s solution (sodium chloride, potassium chloride, calcium chloride and sodium bicarbonate)
- Liquid flow rate = **0.6 ml/hr**
- Nebuliser = Burgener X-175 Enhanced parallel path (Liquid capillary: 175 µm ID)
- Aerosol collection = 5 ml solution for **30 minutes**; tubing length from quartz = 10 cm
- Plasma = lowest stable operating power

- Plasma = 3.0 mm / 2.0 mm ID
- Power = RF 80 W (0 W reflected power)
- Gas = Nebuliser 1.0 SLM Ne & Shroud 3.5 SLM He

Additional Information
- Estimated $10^5$ droplets per second & 300 bacteria per second
- (10^5 per 30 minutes)
- Transit time: gas flow dependant
- (single transit of bacteria in droplet through stable plasma = 40 µs)
### Experimental Conditions

<table>
<thead>
<tr>
<th>Condition</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive Control</td>
<td>Untreated <em>E. coli</em> (same concentration)</td>
</tr>
<tr>
<td>A1</td>
<td>Initial Aerosolised Ringer’s solution before any <em>E. coli</em></td>
</tr>
<tr>
<td>BA</td>
<td>Aerosolised <em>E. coli</em> in Ringer’s solution (no plasma)</td>
</tr>
<tr>
<td>BAP80</td>
<td>Aerosolised <em>E. coli</em> in Ringer’s solution, transported through plasma operating at <strong>80 W</strong></td>
</tr>
<tr>
<td>A2</td>
<td>Final Aerosolised Ringer’s solution after all <em>E. coli</em></td>
</tr>
<tr>
<td>Negative Control</td>
<td>Untreated growth media (no <em>E. coli</em>)</td>
</tr>
</tbody>
</table>

- System ‘flushed’ with 70% Ethanol in-between each aerosolised solution to eliminate carryover
- All residual Ethanol removed using gas flow (10 min) before commencement of next aerosol
<span><p><strong>Agar Plate Colony Counts</strong></p></span>

(colony forming units per millilitre – cfu/ml)

- Control sample before / after consistent therefore cell count reduction is due to plasma/aerosolisation treatment
- Sterile condition maintained (aerosol without bacteria)
- Aerosolisation = 3 log reduction
- Minimal further reduction of recovered viable Plasma-treated cells
- ‘Gentle’ plasma treatment achieved
Bacteria Growth Curve

**Lag Phase:** The delay before growth (Adaptation, Repair, Transcription, Translation)

**Exponential Phase:**
Cell division at a constant rate (mid-exponential)

**Stationary Phase:**
Conditions become unfavourable for growth; no net increase in cell number

**Principle:** Number of cells in suspension $\propto$ Optical Density of an incubated bacterial suspension
Optical Density Measurement at 600 nm

- Positive Control Mean
- Bacteria Aerosol Mean
- Bacteria Aerosol Plasma Mean
- Negative Control Mean

Optical Density (600 nm) vs. Time (Hours)
Lag Phase

- **Corrected**: Negative control data at each time point subtracted from positive control, BA and BAP data
- No lag phase in positive control
- ~5.5 hr BA
- ~8.0 hr BAP
**Exponential Phase**

**Doubling Time:**
The time taken for optical density of culture to increase from 0.5 to 1.0

<table>
<thead>
<tr>
<th>Sample</th>
<th>Doubling Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Positive Control</td>
<td>288</td>
</tr>
<tr>
<td>Bacteria Aerosol</td>
<td>324</td>
</tr>
<tr>
<td>Bacteria Aerosol Plasma</td>
<td>342</td>
</tr>
</tbody>
</table>
Conclusions

• Single bacteria in droplet
• Most droplets “empty”
• Each bacteria/droplet receives same plasma treatment
• No shadowing
• Limited increase in temperature

• The experimental work has shown that aerosolised plasma-exposed cells can survive the treatment with cell structure intact (Gram stain) and they remain viable (agar plate colony counts & growth curves)

• This offers a unique opportunity to study individual bacteria cells’ repair mechanisms of sub-lethal damage (lag phase)

• Viable but non-culturable (VBNC) cells require further investigation
Acknowledgements

- Viable transport of aerosol through microplasma
- Preliminary results on
  - Size & velocity distributions
  - Evaporation
  - Chemistry
  - Charge
  - Plasma - Bacteria interactions

Thank You