Supplementary Information

Non-Faradaic Impedance Characterization of an Evaporating Droplet for Microfluidic and Biosensing Applications

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S1. Geometry dependence of circuit components:

a) **Geometric Capacitance $(C_{geo}(\theta))$:** For a parallel plate system, the geometric (dielectric) capacitance is given by $C_{geo} = A\varepsilon/d$ where A is the area of the electrodes, ϵ permittivity of the medium separating the electrodes and d the separation between the electrodes. This results from the solution of Poisson equation and is determined by the ratio of charge Q on the electrode and voltage V between the electrodes. For any given contact angle θ , the geometrical capacitance can be determined in similar way. We solve for the Poisson equation $(-\vec{\nabla}.(\varepsilon\vec{\nabla}\phi) = 0)$ within the droplet with the boundary condition $\phi = \pm V_e$ at the two electrodes using Sentaurus, An Advanced Device Simulator[1]. . The capacitance is given by $C_{geo} = Q/V_e = \int_{\Omega_e} \varepsilon \vec{E}.d\vec{S} /2V_e$ where $\vec{E}$ is the electric field at the surface of the electrode. Ω_e denotes the surface of the electrode. SFig. 1(a) shows the plot of the geometric capacitance as a function of contact angle θ of droplet with the surface.

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We can generalize this solution for any droplet size (H_z) in z direction, by defining $C_{geo} = H_z\, \varepsilon/g(\theta)$ where $g(\theta)$ is dependent on the droplet shape. For a parallel plate capacitor, $g = d/W$ where W is the width of the electrodes and d the separation between them. Geometry factor can be interpreted as $g = \frac{H_z V}{\int_{\Omega_e} \vec{E}.d\vec{S}}$. SFig. 1 (b) shows the dependence of geometry function of the droplet contact angle (θ). This definition of geometry factor would be useful in evaluation of series resistance which is discussed later. Note, that C_{geo} would be only impedance component of the droplet if it is non-conducting (which is dominant at high frequency when the ions don't respond to the ac signal). However, when electrolyte is conductive (at low/intermediate frequency), the solution will also have a double layer capacitance and series resistance which are discussed next.

b) **Double Layer Capacitance ($C_{dl}(\theta)$)** : An electrode in contact with electrolyte forms a layer of surface ionic charge near its surface. This results in a formation of a diffuse layer due to columbic attraction to the surface charge. This double layer results in a net capacitance, $C_{dl} = \left(\frac{1}{C_S} + \frac{1}{C_{diff}}\right)^{-1}$ where C_S is called stern capacitance and C_{diff} is called the differential capacitance. If the debye length is much larger than the thickness of the stern layer than, $C_S \gg C_{diff}$, so that $C_{dl} \approx C_{diff}$. For any given contact angle θ, this capacitance, $C_{dl}(\theta)$ is evaluated by solving Poisson equation $-\vec{\nabla}.\left(\varepsilon\vec{\nabla}\phi\right) = \rho = p - n$ where $p(x,y,z)$ and $n(x,y,z)$ is the concentration of positive and negative ions in the solution respectively. Again, the capacitance is evaluated by evaluating the charge on the electrode, Q and differentiating it with respect to electrode voltage, V_e i.e. $C = dQ/dV_e$. SFig. 1(c) shows the variation of capacitance as a function of contact angle θ with $n_0 = 10^{-7}M$ for different applied biases. Also, shown is the plot of C_{dl} vs. θ from the analytic solution of Poisson equation in semi-infinite medium i.e. $C_{dl} = A\sqrt{2\ q^2\varepsilon\frac{n_0}{kT}}\ \cosh\left(\frac{qV_e}{2kT}\right)^2$. The numerical solution is in excellent agreement with the analytic approximation. It can be concluded from the simulation that the double layer capacitance is independent of droplet geometry (different droplet shapes with same ionic

concentration n_0). This is true as long as the droplet dimensions are much larger than the Debye

length $\lambda = \sqrt{\frac{\varepsilon kT}{2n_0 q^2}}$ in the ionic solution (maximum debye length is for pure water $n_0 = 100\ nM$ i.e.

$\lambda \approx 1\ \mu m$). Finally, as the droplet evaporates the concentration of the electrolyte increases $n_i =$

$n_i(\theta(t)) = n_0\ V_0/V(\theta(t))$, which we have accounted for in Section 2.3.
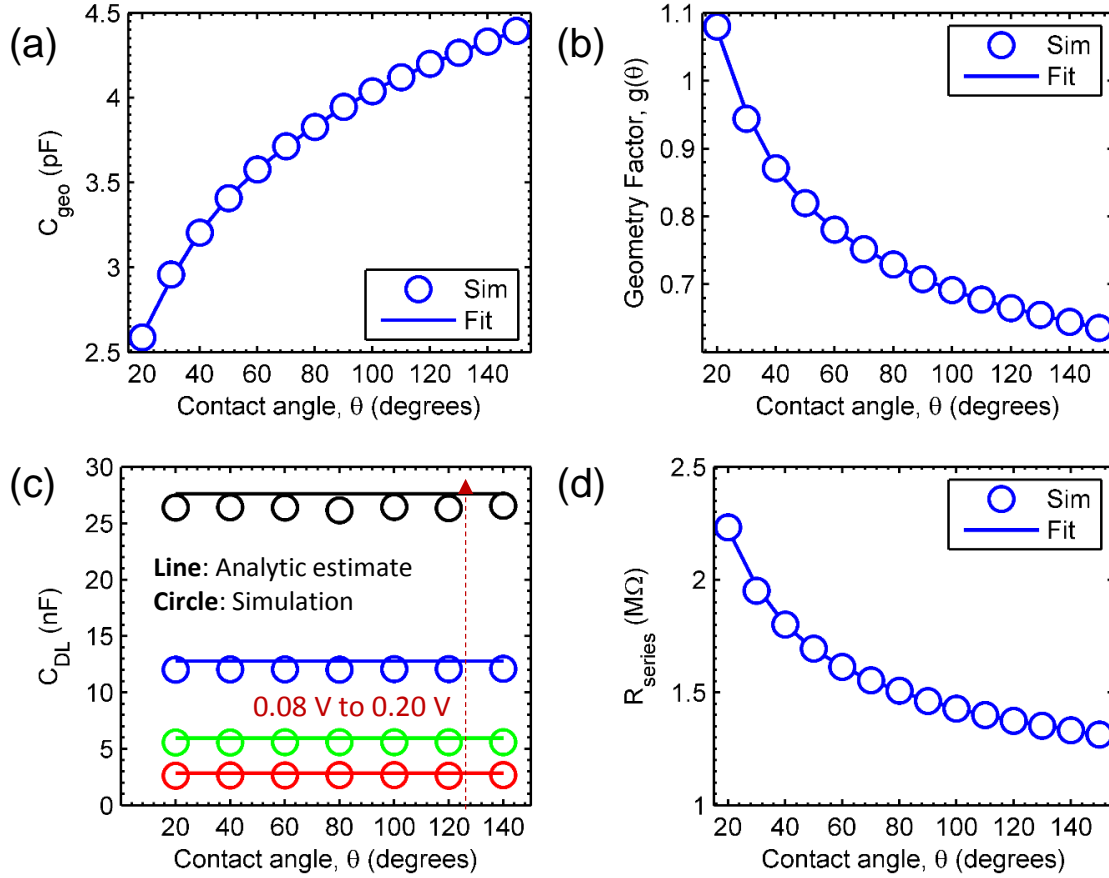
SFig. 1 (a) Geometry capacitance (C_{geo}) as a function of contact angle (θ) (b) Geometry factor (g) as a function of contact angle (θ) (c) Double layer capacitance (C_{DL}) as a contact angle (θ) for different applied bias (V_e) i.e red 0.08 V, green 0.12 V, blue 0.16 V and black 0.20V (circles are from numerical simulation and lines are from analytic estimate) (d) Series resistance (R_{series}) as a function of contact angle (θ) for constant conductivity (σ)

c) **Series Resistance ($R_{series}(\theta)$) :** Series resistance results from potential drop in the solution because

of its finite resistivity. The resistance of a system with two parallel electrodes of area A separated by a

distance d is given by $R_{series} = d/\sigma A$ where $\sigma = qn_i(\mu_n + \mu_p)$ is the conductivity of the solution.

This is result of solution of Poisson equation and evaluation of $R_{series} = \frac{V}{I} == \frac{V}{\int_{\Omega_e} \vec{J}.d\vec{S}}$ where

$\vec{J} = \sigma \vec{E}$ is the current density. This can be related to the geometry factor that we defined earlier as

$R_{series} = \frac{g(\theta)}{\sigma H_z}$. SFig. 1 (d) shows the series resistance dependence on the droplet contact angle (θ).

The conductivity (σ) of the solution is assumed to be constant. Note that in addition to the change in series resistance due to geometry factor $g(\theta)$, there is an additional component $\sigma(\theta(t))$ that comes because of increase concentration of the solution as the droplet evaporates. This is accounted for in the estimation of resistance done in section 2.3.

S2. Description/Derivation of cut-off frequencies:

The net impedance of the system including for the parasitic impedance due to substrate is given by

$Z_{net} = \left(R_{series} + \frac{2}{j\omega C_{dl}} \right) || \left(\frac{1}{j\omega C_{geo}} \right) || \left(Z_{par} \right)$. When parasitic impedance can be represented by a simple

capacitor $i.e.$ $Z_{par} = \frac{1}{j\omega C_{par}}$, the net impedance simplifies to $Z_{net} = \left(R_{series} + \frac{2}{j\omega C_{dl}} \right) || \left(\frac{1}{j\omega (C_{geo}+C_{par})} \right)$.

When double-layer capacitance is the dominant component in impedance, $\frac{2}{\omega C_{dl}} \gg R_{series}$ $i.e.$ $\omega \ll$

$\frac{2}{R_{series}C_{dl}}$. This gives the lower cut-off frequency, $f_{low} = \frac{2}{2\pi R_{series}C_{dl}}$. As f increases beyond f_{low}, R_{series}

starts to dominate, so that $R_{series} + \frac{2}{j\omega C_{dl}} \approx R_{series}$. However, at high enough frequencies,

$\frac{1}{\omega(C_{geo}+C_{par})} \ll R_{series}$, so that $Z_{net} \approx \frac{1}{j\omega(C_{geo}+C_{par})}$. This frequency is such that $\frac{1}{\omega(C_{geo}+C_{par})} \ll R_{series}$

$i.e.$ $f_{high} = \frac{1}{2\pi R_{series}(C_{geo}+C_{par})}$. Intuitively, f_{low} and f_{high} represents frequencies at which the phase of

$Z_{net} \approx -45°$.

S3. Effect of dielectric layer covering electrodes:

In our analysis, we assumed that the dc bias across the electrodes is small so that the faradaic current components are negligible. However, if the device has to be operated at high dc biases in non-faradaic regime, we must cover the electrodes with dielectric coating to block any charge transfer between the electrode and the electrolyte. The effect of dielectric layer can effectively be incorporated in our model by putting a constant capacitor (impedance if the layer is conductive as well) in series with Z_{drop} at each of the electrode ends. For a dielectric layer of thickness t_{layer}, the capacitance of the dielectric layer is given by $C_{layer} = \frac{A\varepsilon_{layer}}{t_{layer}}$ where ε is the dielectric constant of the coating. The net impedance of the system is then given by $Z_{net} = \left(\frac{2}{j\omega C_{layer}} + \left(\left(R_{series} + \frac{2}{j\omega C_{dl}} \right) || \left(\frac{1}{j\omega C_{geo}} \right) \right) \right) || Z_{par}$. However, for physiological ionic concentrations (~$100\ mM$), the double layer capacitance $C_{dl} \geq A\frac{\varepsilon_w}{\lambda_d} \gg A\frac{\varepsilon_w}{t_{layer}}$. This is because $\lambda_d \sim 1nm$ (at $100\ mM$) and water has a very high dielectric constant as compared to dielectric coatings. This will deteriorate the sensitivity of the sensor at low frequency regimes since $Z_{net} \approx \frac{2}{j\omega C_{dl}} + \frac{2}{j\omega C_{layer}} \approx \frac{2}{j\omega C_{layer}}$ is independent of the droplet characteristics. Also, note that the double layer capacitance in this particular case is given by $C_{dl} = A\sqrt{2\ q^2 \varepsilon_w \frac{n_0}{kT}} \cosh\left(\frac{q\psi_{DL}}{2kT} \right)$ where we have replaced the electrode voltage (V_e) by the potential drop (ψ_{dl}) across the electrode. ψ_{DL} must now be obtained by solving for dc operating point of simple voltage divider with C_{layer} and C_{dl} as the two capacitance. By charge conservation,

$$Q_m + Q_{dl} = 0$$

where Q_m is charge on the metal electrode and $Q_{dl} = -\sqrt{8\varepsilon_w kT\ n_0}\ \sinh\left(\frac{q\psi_{dl}}{2kT} \right)$ is the charge in the double layer. Since; $Q_m = C_{layer}V_{layer} = C_{layer}(V_e - \psi_{dl})$, where V_{layer} is the voltage drop across the dielectric layer. An implicit equation for ψ_{dl} in terms of known variables is obtained which can be solved using any nonlinear equation solver.

S4. Determining the diffusion flux through diffusion equivalent capacitance:

The flux of liquid vapor molecules away from the droplet is given by $\Phi_D = \int_\Omega \vec{J}.d\vec{S}$ where $\vec{J} = -D\vec{\nabla}c$ is the outward flux density at the droplet surface. We need to determine the integral such that $\vec{\nabla}.(\vec{\nabla}c) = 0$ subject to the boundary condition that surface concentration of the vapors is c_s and that far away from the droplet is c_∞. This problem is analogous to solving for the electrical charge $Q = \int_\Omega \vec{P}.d\vec{S}$ with $\vec{P} = \epsilon\vec{E}$. This can simply be related to the capacitance (C_E) of the system and potential difference between the surface (ψ_s) and far away from the surface (ψ_∞), $i.e.$ $Q = C_E(\psi_s - \psi_\infty)$. From the equivalence between the electrical system and the molecular diffusion system as shown in table below, we arrive at the evaporation flux $\phi_D = C_D(c_s - c_\infty)$.

STable 1 Equivalence between electrostatics and molecular diffusion system	
Electrostatics	**Molecular diffusion**
ψ	c
ε	D
$\vec{\nabla}.(\vec{\nabla}\psi) = 0$	$\vec{\nabla}.(\vec{\nabla}c) = 0$
$\vec{P} = \epsilon\vec{E} = -\varepsilon\vec{\nabla}\psi$	$\vec{J} = -D\vec{\nabla}c$
$Q = \int_\Omega \vec{P}.d\vec{S} = -\int_\Omega \varepsilon\vec{\nabla}\psi.d\vec{S} = C_E(\psi_s - \psi_\infty)$	$\Phi_D = \int_\Omega \vec{J}.d\vec{S} = -\int_\Omega D\vec{\nabla}c.d\vec{S} = C_e(\phi_s - \phi_\infty)$
$C_E = f(\varepsilon)$	$C_D = f(D)$
where the equivalence holds for any arbitrary function $f(x)$.	

S5. Verification with experimental data:
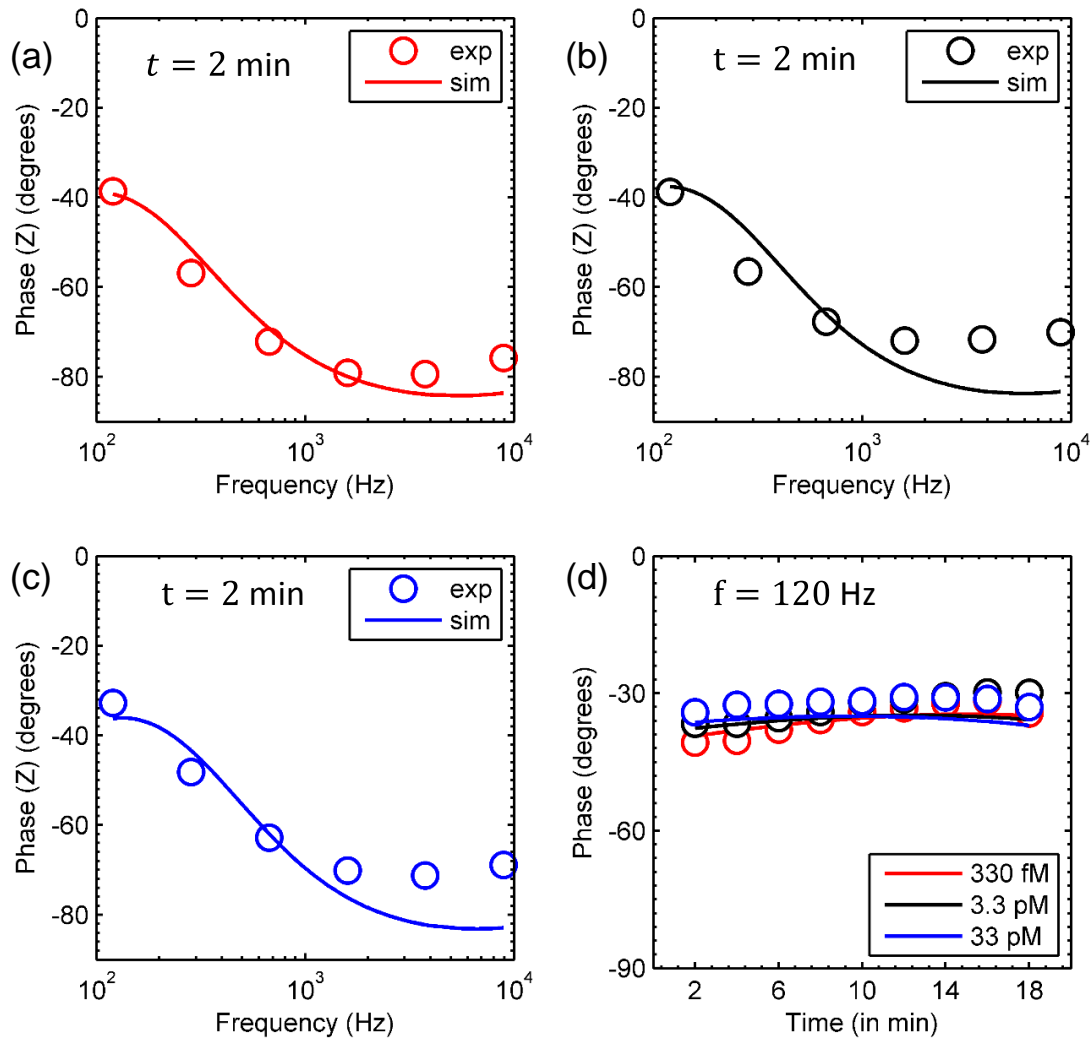
SFig. 2 Phase of impedance (calibration curves) vs. freqeuncy at t = 2 min for different DNA concentration (a) 330 fM, (b) 3.3 pM and (c) 33 pM. (d) Phase of impedance vs. Time for different DNA concentration: 330 fM (red), 3.3 pM (black) and 33 pM (blue).

STable 2 : <u>Tables of physical constants</u>

Parameter	Value	Reference
Mobility of Na^+ ions in water	$5.1 \times 10^{-4} cm^2/Vs$	3
Mobility of Cl^- ions in water	$7.6 \times 10^{-4} cm^2/Vs$	3
Mobility of H^+ ions in water	$3.0 \times 10^{-3} cm^2/Vs$	3
Mobility of OH^- ions in water	$2.0 \times 10^{-3} cm^2/Vs$	3
Permittivity in free space	$8.85 \times 10^{-14} F/cm$	4
Relative permittivity of water	78.9	5
Density of water	$1 g/cm^3$	6
Saturation vapor density of water in air at room temperature	$\sim 2.1 \times 10^{-5} g/cm^{-3}$	7
Diffusion constant for water vapor in air at room temperature	$\sim 0.2 cm^2/sec$	7
Humidity factor, $(c_s - c_\infty)/c_s$	0.60	-
Ionic concentration of free H^+/OH^- ions in pure water	$10^{-7} M$	-
Thickness of stern layer	$0.4 nm$	8

STable 3: <u>Table of geometry parameters</u>

Parameter	Value
Electrode width (W)	$400 \mu m$
Electrodes separation (L)	$20 \mu m$
Length of electrode in contact with solution (H_z)	$4 mm$
Initial angle of the droplet with the substrate (θ_0)	$130°$
Droplet contact width (r)	$400 \mu m$
Effective area for double layer capacitance (A)	$0.21 cm^2$

STable 4: <u>Equations</u>

Time dynamics of droplet evaporation
$$\Phi_m = \int \vec{J}.d\vec{S}$$ $$\vec{J} = -D\vec{\nabla}c$$ $$\Phi_m = -\frac{dm}{dt} = -\text{P}\frac{dV}{dt}$$ $$V(\theta) = r^2 H_z \left(\frac{\theta}{sin^2\theta} - \frac{cos\theta}{sin\theta}\right)$$ $$R_s(\theta) = r/\sin(\theta)$$ $$\frac{d\theta}{dt} = -\frac{D(c_s - c_\infty)}{\text{P}r^2}\frac{(\theta \sin^2\theta)}{1 - \theta \cot\theta}\left(1 + \frac{0.3069}{\alpha} + \frac{0.2717}{\alpha^2}\right)\frac{1}{\alpha} = -\lambda f(\theta, r, H_z)$$

<u>Geometry dependence of circuit components</u>	
Series Resistance/Conductance	$$R_{series} = \frac{1}{\sigma}\frac{g(\theta)}{H_z}$$ $$\sigma = qn_i(\mu_p + \mu_n)$$ $$G_{series} = 1/R_{series}$$
Double Layer Capacitance	$$C_{dl} = \left(\frac{1}{C_S} + \frac{1}{C_{diff}}\right)^{-1}$$ $$C_{diff} = A\sqrt{\frac{2q^2\varepsilon n_i}{kT}}\cosh\left(\frac{qV_e}{2kT}\right)$$ $$C_S = \frac{A\varepsilon_w}{d_S}$$
Geometry Capacitance	$$C_{geo} = H_z\frac{\varepsilon}{g(\theta)}$$

<u>Time dependence of circuit components</u>	
Series Resistance	$$R_{series} = \frac{\left(1 - \frac{t}{T}\right)^n g(t)}{\sigma_0 V_0 H_z}$$ $$G_{series} = \frac{1}{R_{series}}$$
Double Layer Capacitance	$$C_{DL} = C_{DL,0}/\left(1 - \frac{t}{T}\right)^{n/2}$$ $$C_{DL,0} = A\sqrt{\frac{2q^2\varepsilon n_0}{kT}}\cosh\left(\frac{qV_e}{kT}\right)$$
Geometry Capacitance	$$C_{geo} = H_z\frac{\varepsilon}{g(t)}$$

STable 5: Definition of symbols

Net impedance (admittance) of the system	Z_{net} (Y_{net})
Droplet impedance (admittance)	Z_{drop} (Y_{drop})
Warburg impedance	Z_w
Double layer impedance	Z_{dl}
Parasitic impedance	Z_{par}
Series resistance (conductance)	R_{series} (G_{series})
Double layer capacitance	C_{dl}
Differential capacitance	C_{diff}
Stern capacitance	C_S
Stern layer thickness	d_s
Geometry (i.e. dielectric) capacitance	C_{geo}
Charge transfer resistance	R_{ct}
Frequency (Angular Frequency)	f (ω)
Lower and higher cut-off frequencies	f_{low}, f_{high}
Time	t
Sensitivity of the sensor at time t	$S(t)$
Amplification in sensitivity at time t relative to $t = 0$	$\alpha(t)$
Applied DC bias	V_{dc}
Applied AC bias	V_{ac}
Concentration of chemical/biomolecules	ρ
Initial concentration of ions in the droplet	n_0

Concentration of ions at time t	$n_i(t)$
Width of electrodes	W
Length of electrodes	H_E
Length of cylinderical segment of droplet	H_z
Seperation between electrodes	L
Contact width of droplet	r
Contact angle of drolet with the substrate	θ
Initial volume of droplet	V_0
Volume of droplet at times t	$V(t)$
Geometry factor at time $t = 0$	g_0
Geometry factor	$g(t)$
Solution conductivity	σ
Mobility of positive and negative ions	μ_p, μ_n
Diffusion capacitance of truncated cylinder of finite size	C_D
Saturation vapor concentration of liquid	c_s
Diffusion constant for liquid vapors in ambient surroundings	D
Density of the liquid composing the droplet	P

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