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**ELECTRONICS SUPPORTING INFORMATION**

# Towards a unified description of the charge transport mechanisms in conductive atomic force microscopy studies of semiconducting polymers

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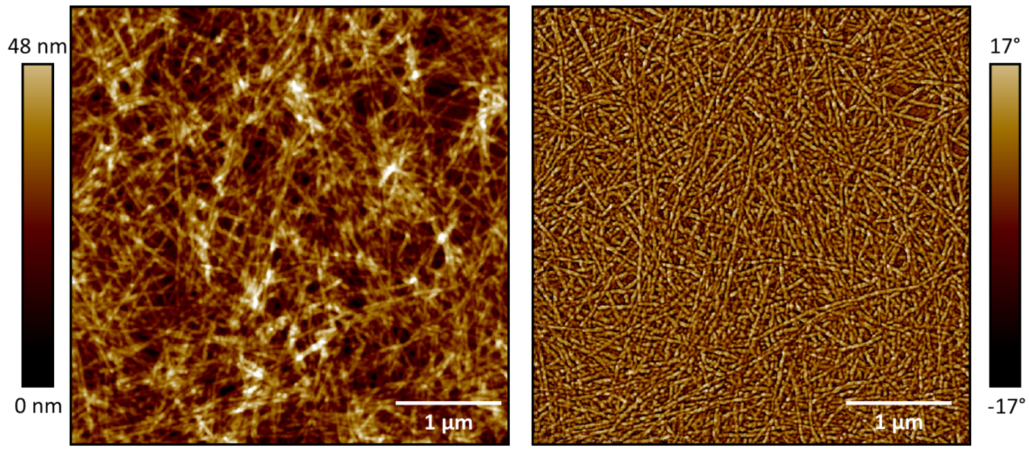
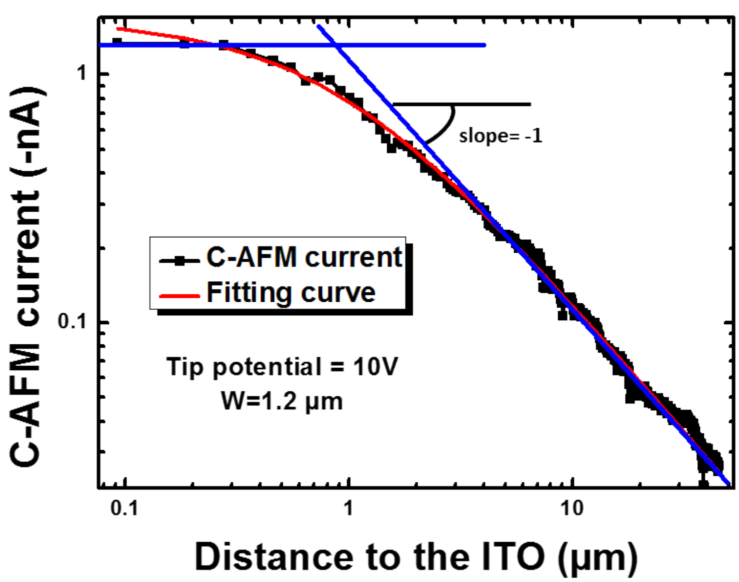
**Supporting Information 1**

Height and phase tapping-mode AFM images obtained on a fibrillate P3Ht thin film.




**Supporting Information 2**

C-AFM current profile obtained with a dc sample bias of -10 V for a high aspect ratio channel (w = 1.2 µm, L > 30 µm). The blue lines correspond to the behaviour expected in the contact and transport resistance dominating regimes. The red curve represents the fitting curve of the c-AFM profile with the expression: $= \frac{V}{\frac{\rho_{loc}}{\alpha.d} + \frac{\rho_{film.L}}{w.t}}$, leading to an extracted value of $\rho_{film} = 4500\ \Omega cm$.



**Supporting Information 3**

Derivation of the analytical I-V expression for a point contact configuration and radial injection of carriers

$\vec{E} = -\, gr\vec{a}d\; V = -\, \partial V/\partial r \cdot \vec{r}$

Poisson's Equation

$$div\, \vec{E} = \frac{\rho}{\varepsilon_r \varepsilon_0} = \frac{ep}{\varepsilon_r \varepsilon_0}$$

($\rho$ = charge distribution, $p$ = carrier density)

Ohm's law

$$J = \sigma E = e\mu p E$$

Steady state conditions of radial injection of carriers and flow across a hemisphere of radius r

$$I = 2\pi e\mu p r^2 E_r = cst$$

(Lampert et Mark, Current Injection in Solids Academic Press, New-York, 1970, eq. 8.1, page 159)

$$p = \frac{I}{2\pi e\mu r^2 E_r}$$

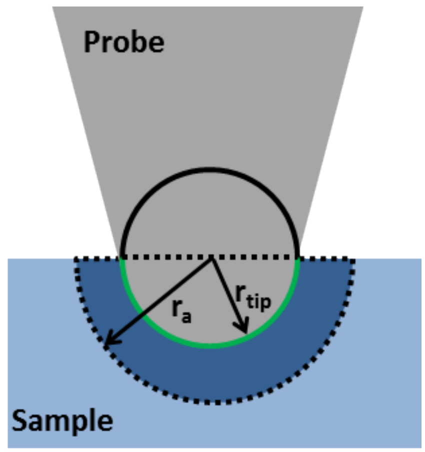
Combining Poisson's equation and Ohm's law leads to

$$div\, \overline{E} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 E_r\right) = \frac{ep}{\epsilon_0 \epsilon_r}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 E_r\right) = \frac{e}{\epsilon_0 \epsilon_r}\frac{I}{2\pi e\mu r^2 E_r}$$

$$r^2 E_r \frac{\partial}{\partial r}\left(r^2 E_r\right) = \frac{I r^2}{2\pi\mu\epsilon_0\epsilon_r}$$

<u>Case 1:</u> half-buried tip inside the polymer film as shown in the Figure below:




$r_c$ is the radius of the equivalent half buried sphere at the tip-sample contact and $r_a$ is the radius of the hemisphere circumscribing the volume beneath the probe where charges accumulates

Integrating both terms of the previous equation between $r_{tip}$ and r

$$\int_{r_{tip}}^{r} r^2 E_r \frac{\partial}{\partial r}\left(r^2 E_r\right) dr = \int_{r_{tip}}^{r} \frac{I_0 r^2}{2\pi\mu\epsilon_0\epsilon_r} dr$$

$$u(r) = r^2 E_r \rightarrow \frac{\partial}{\partial r} u^2(r) = 2.u(r) \frac{\partial}{\partial r} u(r)$$

$$\int_{r_{tip}}^{r} r^2 E_r \frac{\partial}{\partial r}\left(r^2 E_r\right) dr = \frac{1}{2}\left(r^2 E_r\right)^2 = \frac{I_0}{2\pi\mu\epsilon_0\epsilon_r} \frac{\left[r^3\right]_{r_{tip}}^{r}}{3}$$

$$E_r = \sqrt{\frac{I_0}{3\pi\mu\epsilon_0\epsilon_r}} \sqrt{\frac{r^3 - r_{tip}^3}{r^4}}$$

$$V = \int_{r_c}^{r_a} E_r dr = \sqrt{\frac{I_0}{3\pi\mu\epsilon_0\epsilon_r}} \int_{r_{tip}}^{r_a} \sqrt{\frac{r^3 - r_{tip}^3}{r^4}} dr$$

$$A = \sqrt{\frac{I_0}{3\pi\mu\epsilon_0\epsilon_r}}$$

$$V = A \int_{r_{tip}}^{r_a} \sqrt{\frac{r^3 - r_{tip}^3}{r^4}} dr = A \int_{r_{tip}}^{r_a} \frac{1}{\sqrt{r}} \sqrt{1 - \frac{r_{tip}^3}{r^3}} dr$$

1[st] approximation: $r_{tip} << r_a$

$r_{tip} < r < r_a$ $\qquad$ $\frac{r_{tip}}{r} < 1$ $\qquad$ $x = \frac{r_{tip}^3}{r^3} < 1$

$$(1 - x)^\alpha = 1 + \sum_{n=1}^{\infty} \frac{\alpha(\alpha - 1)...(\alpha - n + 1)}{n!} ( - 1)^n x^n$$

for $x \in ] - 1;1[$ and $n \in N$

$$V = A \int_{r_{tip}}^{r_a} \frac{1}{\sqrt{r}} (1 + \sum_{n=1}^{\infty} \frac{1/2(1/2 - 1)...(1/2 - n + 1)}{n!} ( - 1)^n \left(\frac{r_{tip}}{r}\right)^{3n}) \cdot dr$$

$$V = A \int_{r_{tip}}^{r_a} \frac{1}{\sqrt{r}} \cdot dr + A(\int_{r_{tip}}^{r_a} \frac{1}{\sqrt{r}} \sum_{n=1}^{\infty} \frac{1/2(1/2 - 1)...(1/2 - n + 1)}{n!} ( - 1)^n \left(\frac{r_{tip}}{r}\right)^{3n}) \cdot dr$$

$$V = A \int_{r_{tip}}^{r_a} \frac{1}{\sqrt{r}} \cdot dr + A(\sum_{n=1}^{\infty} \frac{1/2(1/2 - 1)...(1/2 - n + 1)}{n!} ( - 1)^n \int_{r_{tip}}^{r_a} \frac{1}{\sqrt{r}} \left(\frac{r_{tip}}{r}\right)^{3n}) \cdot dr$$

$$V = 2A\left(\sqrt{r_a} - \sqrt{r_{tip}}\right) + A(\sum_{n=1}^{\infty} \frac{1/2(1/2 - 1)...(1/2 - n + 1)}{n!} ( - 1)^n {r_{tip}}^{3n} \int_{r_{tip}}^{r_a} \frac{1}{r^{3n + 1/2}}) \cdot dr$$

$$V = 2A(\sqrt{r_a} - \sqrt{r_{tip}}) + A(\sum_{n=1}^{\infty} \frac{{}^1/_2({}^1/_2 - 1)...({}^1/_2 - n + 1)}{n!}(-1)^n {r_{tip}}^{3n} \cdot \left[\frac{r^{-3n+{}^1/_2}}{-3n+{}^1/_2}\right]_{r_{tip}}^{r_a})$$

$$V = 2A(\sqrt{r_a} - \sqrt{r_{tip}}) + A(\sum_{n=1}^{\infty} \frac{{}^1/_2({}^1/_2 - 1)...({}^1/_2 - n + 1)}{n!}(-1)^n \frac{\sqrt{r_{tip}}}{-3n+{}^1/_2}\left[\left(\frac{r_{tip}}{r_a}\right)^{3n-{}^1/_2} - 1\right])$$

$$V \approx 2A(\sqrt{r_a}) - A \cdot \sqrt{r_{tip}}(\sum_{n=1}^{\infty} \frac{{}^1/_2({}^1/_2 - 1)...({}^1/_2 - n + 1)}{n!}(-1)^n \frac{1}{-3n+{}^1/_2}) \cdot$$

The second term includes a converging series proportional to $\sqrt{r_{tip}}$ and can be considered as negligible compared to the first term

$$V \approx 2A\sqrt{r_a}$$

$$I_0 \approx \frac{3\pi}{4}\varepsilon_r\varepsilon_0\mu \cdot \frac{1}{r_a}V^2$$

Consistent with Murray A. Lambert and Peter Mark. Academic Press, New York, 1970, Table 8.1, page 163: current flow in a spherical geometry, and Eq. 8.8 page 161.

2nd approximation: $r_{tip} \lesssim r_a$ and $r_a = r_{tip}(1+\varepsilon)$ with $\varepsilon<1$

With $r \in ]r_{tip}, r_a[$ with $r_a \approx r_{tip}$, ie. $r = r_{tip}(1+\varepsilon)$ with $\varepsilon \to 0$

$r^3 = r_{tip}^3(1+\varepsilon)^3 \approx r_{tip}^3(1+3\varepsilon)$ and $r^{-4} = r_{tip}^{-4}(1-4\varepsilon)$

$$E_r = \sqrt{\frac{I_0}{3\pi\mu\epsilon_0\epsilon_r}}\sqrt{\frac{r^3 - r_{tip}^3}{r^4}}$$

$$E_r \approx \sqrt{\frac{I_0}{3\pi\mu\epsilon_0\epsilon_r}}\sqrt{\frac{r^3 - r_{tip}^3}{r^4}} \approx \sqrt{\frac{I_0}{3\pi\mu\epsilon_0\epsilon_r}}\sqrt{\frac{3\varepsilon}{r_{tip}}}$$

$$with\ \varepsilon = \frac{r - r_{tip}}{r_{tip}}$$

$$E_r \approx \sqrt{\frac{I_0}{\pi\mu\epsilon_0\epsilon_r}}\sqrt{\frac{r - r_{tip}}{r_{tip}^2}}$$

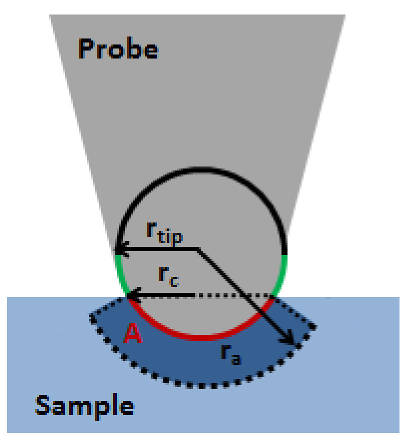
$$V = \int_{r_{tip}}^{r_a} \sqrt{\frac{I_0}{\pi\mu\epsilon_0\epsilon_r}}\sqrt{\frac{1}{r_{tip}^2}}\sqrt{r - r_{tip}}dr = \sqrt{\frac{I_0}{\pi\mu\epsilon_0\epsilon_r r_{tip}^2}}\frac{2}{3}\left[\left(r - r_{tip}\right)^{3/2}\right]_{r_{tip}}^{r_a}$$

$$V^2 = \frac{I_0}{\pi\mu\epsilon_0\epsilon_r r_{tip}^2}\frac{4}{9}\left(r_a - r_{tip}\right)^3$$

$$I_0 = \frac{9}{8}\epsilon_0\epsilon_r\mu\ \frac{2\pi r_{tip}^2}{\left(r_a - r_{tip}\right)^3}V^2$$

Consistent with Murray A. Lampert and Peter Mark. Academic Press, New York, 1970, Table 8.1, page 163: current flow in a quasi-flow case geometry.

Case 2: realistic situation with a smaller indentation of the tip inside the sample leading to $r_c < r_{tip}$, as shown in the Figure below:




The area A of the cap sphere buried in the sample and in contact with the sample is given by

$A = 2\pi r_{tip}\left(r_{tip} - \sqrt{r_{tip}^2 - r_c^2}\right)$

with $\left(r_{tip} - \sqrt{r_{tip}^2 - r_c^2}\right)$ corresponding to the indentation into the film

The steady state conditions of radial injection of carriers and flow across such a cap sphere are

$I = 2\pi e\mu p r(r - \sqrt{r^2 - {r_c}^2})E_r = cst$

Following the derivation described above for a half-buried sphere with $r_{tip} \lesssim r_a$ one yields:

$$E_r \approx \sqrt{\frac{2I}{\pi\mu\epsilon_0\epsilon_r}}\sqrt{\frac{r - r_{tip}}{r_c^2}}$$

Meanwhile the final relation for the current in given by:

$$I = I_0\frac{A}{A_0} = I_0\frac{2\pi r_{tip}\left(r_{tip} - \sqrt{r_{tip}^2 - r_c^2}\right)}{2\pi r_{tip}^2} \approx I_0\frac{1}{2}\frac{r_c^2}{r_{tip}^2}$$ with $r_c < r_{tip}$, therefore

$$I_0 \approx \frac{3\pi}{4}\varepsilon_r\varepsilon_0\mu\frac{1}{r_a}V^2$$ if $r_{tip} << r_a$ becomes $$I \approx \frac{3\pi}{8}\varepsilon_r\varepsilon_0\mu\frac{r_c^2}{r_{tip}^2 r_a}V^2$$

$$I_0 = \frac{9}{8}\epsilon_0\epsilon_r\mu\ \frac{2\pi r_{tip}^2}{\left(r_a - r_{tip}\right)^3}V^2$$ if $r_{tip} \lesssim r_a$ becomes

$$I = \frac{9}{8}\pi\epsilon_0\epsilon_r\mu\ \frac{r_c^2}{\left(r_a - r_{tip}\right)^3}V^2$$

Determination of local carrier density $p_{cont}$, carrier mobility ($\mu$) and probing depth ($r_a$-$r_{tip}$) in small-indentation contact upon fixed bias: steady-state current flowing conditions

Ohm’s law with small indentation contact

$$\frac{I}{\pi.{r_c}^2} \approx J = e\mu.p_{cont}.E$$

From previous derivations

$$E_r(r) \approx \sqrt{\frac{2I}{\pi\mu\epsilon_0\epsilon_r}}\sqrt{\frac{r - r_{tip}}{r_c^2}}$$

And $$I = \frac{9}{8}\pi\epsilon_0\epsilon_r\mu \; \frac{r_c^2}{(r_a - r_{tip})^3}V^2$$

The three equations above lead to

$$p_{cont}(r) = \frac{3}{4}.\frac{\varepsilon_r\varepsilon_0}{e}.V.\frac{1}{(r_a - r_{tip})^{3/2}}.\frac{1}{(r - r_{tip})^{1/2}}$$

with

$$p_{cont}(r = r_a) = \frac{3}{4}.\frac{\varepsilon_r\varepsilon_0}{e}.\frac{1}{(r_a - r_{tip})^2}.V$$

These two equations indicate charge accumulation in the probed volume underneath the tip apex with a depth extension $r_a$-$r_{tip}$. $r_a$ is expected to **increase with the voltage** to satisfy the **boundary condition 1** : $p_{cont}(r = r_a) = p_{film}$ irrespective of V within the voltage range [$V_0$; $V_R$] in which space charge limited current prevails. Experimentally determined: $V_0 = 0.5$ V and $V_R = 1.7$ V. Therefore,

$$p_{film} = \frac{3}{4}.\frac{\varepsilon_r\varepsilon_0}{e}.V.\frac{1}{(r_a - r_{tip})^2} = constant$$

$$r_a - r_{tip} = \sqrt{\frac{3}{4}.\frac{\varepsilon_r\varepsilon_0}{e}.V.\frac{1}{p_{film}}}$$

B is experimentally determined by parabolic fitting of the I-V profile such as

$$\log(I) = 2log(V) + log(B)$$

$$10^B \sim A/V^2 \sim \Omega^{-1}V^{-1}$$

Experimentally determined $10^B = 8.7\ 10^{-11}\ \Omega^{-1}V^{-1}$

This implies

$$\mu = \frac{8}{9\pi}.\frac{10^B}{\varepsilon_r\varepsilon_0}.\frac{(r_a - r_{tip})^3}{{r_c}^2}$$

From the above variations of $r_a$-$r_{tip}$ with the applied voltage

$$\mu = \frac{1}{\sqrt{3}\pi}.\frac{10^B}{{p_{film}}^{3/2}}.\frac{\sqrt{\varepsilon_r\varepsilon_0}}{e^{3/2}}\frac{1}{{r_c}^2}V^{3/2}$$

As expected the mobility also **increases with the voltage** within the SCLC dominating voltage range. At $V = V_0$ the above expression should satisfy **boundary condition 2**:

$$\mu(V = V_0) = \mu_{film}$$

and $\mu_{film} = 1/(e.p_{film}.\rho_{film})$

and $p_{film}$ the constant defined above and $\rho_{film}$ experimentally determined

$$\rho_{film} = 4600\ \Omega.cm$$

Implementing the $r_a$-$r_{tip}$ dependence of V in $p_{cont}(r)$ leads to

$$p_{cont}(r) = \left(\frac{3}{4}.\frac{\varepsilon_r\varepsilon_0}{e}\right)^{1/4}.p_{film}{}^{3/4}.V^{1/4}.\frac{1}{(r - r_{tip})^{1/2}}$$

At a given distance r in the probed volume, the carrier density also **increases with the voltage**.

Combining the two boundary conditions above and the definition of $\rho_{film}$, one obtains

$$p_{film} = \frac{1}{3\pi^2 r_c{}^4}\frac{\varepsilon_r\varepsilon_0}{e}10^{2B}\rho_{film}{}^2\, V_0{}^3$$

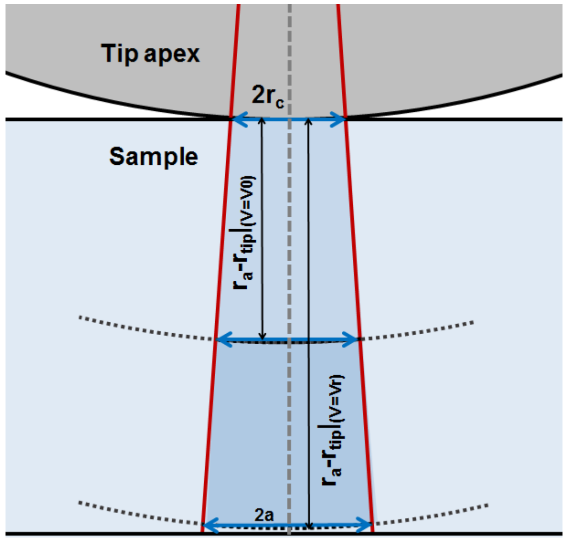
Determination of $r_c$

Finally for $V > V_R$, the I-V profile exhibits a linear variation (Figure 4 (b)), indicating that the SCLC regime no longer dominates the charge transport. Similarly to the SCLC dominating regime, this resistive regime is not affected either by the tip-counter electrode distance, indicating the local character of the dominating transport mechanisms. The narrowness of the contact is expected to imply spreading effect which the corresponding resistance analytical expression is given as follow

$$R_S = \frac{\rho}{4a}$$

With ρ the film resistivity and a the contact radius. Assuming that the spreading effect occurs beyond $r=r_a$ the above equation becomes

$$R_S = \frac{\rho_{film}}{4a} = \frac{\rho_{film}}{4\, r_c\, r_a(V = V_R)}\, r_{tip}$$




$R_S$ = 4.68 GΩ as experimentally determined with $\rho_{film}$ = 4600 Ω.cm, a = 2.46 nm

From above we have

$$r_a - r_{tip} = \sqrt{\frac{3}{4}.\frac{\varepsilon_r \varepsilon_0}{e}.V.\frac{1}{p_{film}}} = \frac{3\pi}{2}.\frac{{r_c}^2}{\rho_{film}.10^B} {V_0}^{-3/2}\sqrt{V}$$

Therefore

$$\frac{r_a(V = V_R) - r_{tip}}{r_a(V = V_0) - r_{tip}} = \sqrt{\frac{V_R}{V_0}}$$

to be developed in

$$\frac{3\pi}{2}\sqrt{\frac{V_R}{{V_0}^3}}\frac{a^2}{\rho_{film}.10^B.r_{tip}}.\left(\frac{r_c}{a}\right)^3 + \frac{r_c}{a} - 1 = 0$$

With $10^B = 8.7\ 10^{-11}\ \Omega^{-1}V^{-1}$; $\rho_{film} = 4600\ \Omega.cm, a = 2.46\ nm$,

$r_{tip} = 25\ nm$ ; $V_0 = 0.5\ V\ and\ V_R = 1.7\ V$ we yield

$r_c = 1.66\ nm$

$p_{film} = 1.57\ 10^{18}\ cm^{-3}$

$\mu_{film} = \mu(V = V_0) = 8.69\ 10^{-4}\ cm^2V^{-1}s^{-1}$ and $\mu(V = V_R) = 5.45\ 10^{-3}\ cm^2V^{-1}s^{-1}$

$r_a(V = V_0) - r_{tip} = 6.51\ nm$ and $r_a(V = V_R) - r_{tip} = 12\ nm$

$E(V = V_0) = 77\ 10^6\ V\ m^{-1}$ and $E(V = V_R) = 142\ 10^6\ V\ m^{-1}$

Average carrier density in the locally probed volume underneath the probe

$$\langle p_{cont} \rangle = \frac{1}{r_a - r_{tip}} \int_{r_{tip}}^{r_a} p_{cont}(r).dr = \frac{3}{4}.\frac{\varepsilon_r \varepsilon_0}{e}.V.\frac{1}{(r_a - r_{tip})^2} = 2.p_{film}$$

Irrespective of V, $\langle p_{cont} \rangle = 3.18\ 10^{18} cm^{-3}$

The space charge limited current regime is only observed in the [0.5 V; 1.7 V] voltage range. From the above model this corresponds to the following variations of $r_a$, μ and $\langle p_{cont} \rangle$

| **V (V)** | 0.5 | 1.2 | 1.7 |
|---|---|---|---|
| **$r_a$-$r_{tip}$ (nm)** | 6.51 | 10.08 | 12.00 |
| **μ ($cm^2.V^{-1}.s^{-1}$)** | $8.69\ 10^{-4}$ | $3.23\ 10^{-3}$ | $5.45\ 10^{-3}$ |
| **$\langle p_{cont} \rangle$ ($cm^{-3}$)** | $3.14\ 10^{18}$ | | |

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