Explaining the Transition from Diffusion Limited to Reaction Limited Surface Assembly through Spatial Variations

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Surface Preparation, tSPL Patterning, and Experimental Details:

Sample Preparation:

Polymer material and polymer samples were prepared as previously described[1]. We show the polymer structures and sample layout in figure S1.

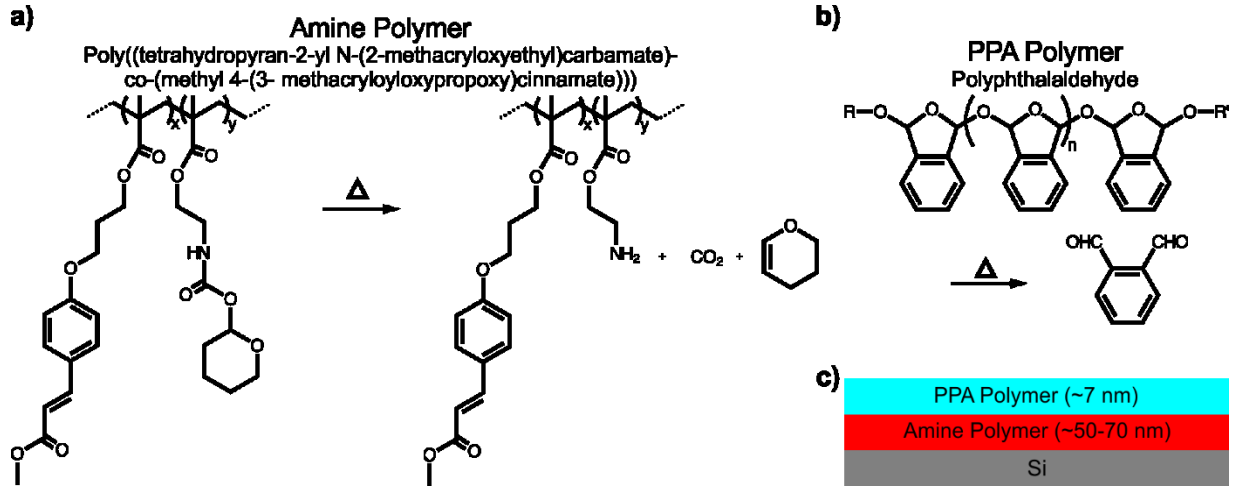

Figure S1. a) Chemical structure of the amine polymer. Under applications of heat, the tetrahydropyran group cleaves, leaving behind an exposed functional amine group. **b)** Chemical structure of the PPA passivating layer. When heated, this polymer decomposes from its polymer form to its monomeric units. **c)** Schematic showing the layering of the polymer materials along with the polymer layer thicknesses.

Briefly, silicon samples were cut to 1 in x 1 in pieces. They were sonicated with a 5% Triton X solution for 30 minutes, followed by rinsing with warm water. They were then sonicated with

de-ionized H_2O for 30 minutes, followed by rinsing with Ethanol. Finally, they were sonicated with ethanol for 30 min, rinsed with Ethanol and dried with Nitrogen. The samples were then placed in a Plasma Asher (TePla 100-E Plasma System) for 2 minutes.

After the samples were cleaned, a solution of the amine polymer (20 mg/mL) was spun-cast onto the samples (1000 RPM, ACC 1500, 2 minutes). The samples were then placed under a UV lamp for 1 hour for cross-linking.

Upon completion of cross-linking, a solution of PPA polymer (0.5% by weight) was spun-cast on top of the samples (5798 RPM, ACC 1500, 80 seconds).

Simulation Details:

All simulations were done in Matlab.

To simulate Brownian motion, particles were subject to the high friction limit of the Langevin equations with only the Brownian force acting on the particles which for 1-D goes as:

$$\dot{x} = \Gamma(t) \tag{S1}$$

where

$$< \Gamma(t) > = 0$$

$$< \Gamma(t)\Gamma(t') > = 2D\delta(t - t')$$

Where D is the diffusion constant ($2.4 \cdot 10^{-11}$ m^2/s). We note that because we leave out the inertia terms, there may be additional effects which are not taken into account in the models and physical understanding presented in the manuscript. We assume $\Gamma(t)$ is Gaussian distributed.

We introduce a mean free time, $\tau = 10^{-6}\ s$, to expedite the simulation and to facilitate our understanding the return distribution function discussed below. Given this mean free time, our particles have an effective mean free path (MFP) of ~12 nm. We define a MFP here as $\sqrt{6D\tau}$. Though this is large in comparison to real MFP, the results shown in this work are independent of the MFP.

In figure S2, we show the 3-D mean squared displacement of an ensemble of particles for ten seconds. As expected for high friction case, the mean squared displacement is linear in t.

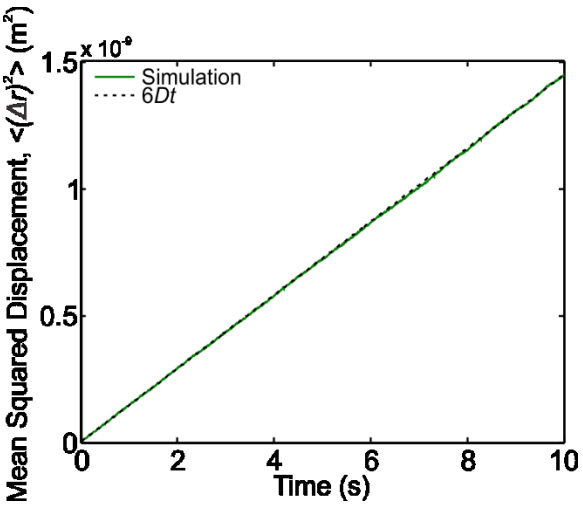

Figure S2. Simulation of 3-D motion of an ensemble of particles (10^5) as a function of time. As expected the mean squared displacement is linear in time.

Calculation of r_d

The return rate, r_d, can be estimated by computing the total number of particles expected to hit the surface over a given mean free time, τ. The areal density of particles in a wedge of thickness dz at a distance z_o away from the surface is given by:

$$\sigma = c_o dz$$

(S2)

Where c_o is the bulk concentration (in the simulation: c_o~10^{18} particles/m^3). The percentage of particles, p_s, at a height z_o from the surface that will over a time step τ strike the surface is given by:

$$p_s(z_o) = \frac{1}{\sqrt{2\pi k_b T}} \int_{z_o/\tau}^{\infty} dv \left[e^{-\frac{mv^2}{2k_b T}} \right] = \frac{\sqrt{\tau}}{\sqrt{4\pi D}} \int_{z_o/\tau}^{\infty} dv \left[e^{-\frac{\tau v^2}{4D}} \right]$$

(S3)

Where k_b the Boltzmann constant and T is the temperature. The right hand sides of equation S3 is written for the notation used in our simulations. The total areal density of particles that will strike the surface over a time step τ is then given by:

$$\Sigma = \int_0^{\infty} dz [p_s(z_o) c_o]$$

(S4)

Where we have integrated over all possible values of z_o. Equation S4 can be simplified using a simple integration by parts, the result is:

$$\Sigma = c_o \frac{\sqrt{D\tau}}{\sqrt{\pi}}$$

(S5)

Finally, to calculate the rate, we divide equation S5 by the time step τ returning and integrate over the area of the patch:

$$r_d = c_o \frac{\sqrt{D\pi}}{\sqrt{\tau}} R^2$$

(S6)

Where R is the patch radius (R=1 μm in the simulations). For a 1 μm circular patch r_d~8700 particles/s. Simulations give a value of ~8300 particles/s on the patch. We note with equation S6, if we allow the mean free time to approach in the limit of $\tau \to 0^+$, the return rate diverges. This limit is also the diffusion equation, which typically shows the planar depletion diverging. Just as with the spatial divergence, the temporal divergence disappears when the mean free path is taken into account.

Calculation of the temporally averaged Return Displacement Distribution:

In this section, we are concerned with an approximation for the temporally averaged Return Displacement distribution Function (tRDF). As the name suggests, the tRDF is the average lateral displacement a particle has when it returns to the surface it started on (figure S3).

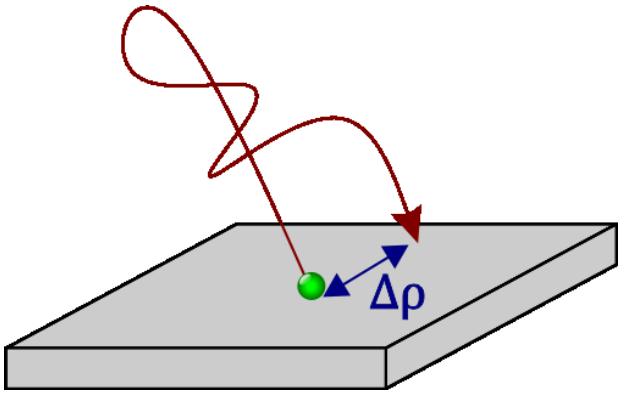

Figure S3. Schematic showing a particle that leaves the surface and eventually returns some lateral displacement ($\Delta\rho$) away.

To calculate the tRDF, we break the problem into three distinct stages: average lateral and average surface displacement distance (z') with some small initial offset, the return time distribution to come back from the surface displacement distance, and finally the average lateral displacement while in transit back to the surface.

Given that our particles start at the origin and have mean free travel time, τ, we know the initial average lateral and average surface displacement distance can be estimated from the fundamental solution of the diffusion equation as:

$$f_1 = \frac{2}{(4\pi D\tau)^{3/2}} e^{\frac{-\left(x'^2+y'^2+z'^2\right)}{4D\tau}}$$

(S7)

The return time distribution is a bit harder because we have imposed a mean free time, it will be somewhere between the continuous and the discrete case discussed in the manuscript. In order to approximate the profile, we use the continuous distribution given by:

$$f_2 = \frac{z'}{\sqrt{4\pi D t^3}} e^{-\frac{z'^2}{4Dt}}$$

(S8)

Where t is now measured relative to τ. Finally, using the same relative time, we can use the fundamental solution of the diffusion equation to calculate the final lateral displacement (given by (x, y)) from its initial lateral displacement (given by (x', y')) as:

$$f_3 = \frac{1}{4\pi D t} e^{\frac{-\left((x-x')^2+(y-y')^2\right)}{4Dt}}$$

(S9)

Summing over all possible initial displacement values for (x', y', z') and averaging over time, we can compute the tRDF as:

$$f_{tot}(x, y) = \int dx' \left[\int dy' \left[\int dz' \left[\int dt [f_1 f_2 f_3]\right]\right]\right]$$

(S10)

Plugging and rearranging terms from equation S7-S9, we can re-write equation S10 as:

$$f_{tot}(x, y) = \frac{8\pi D}{(4\pi D\tau)^{3/2}} \int dx' \left[\int dy' \left[e^{\frac{-\left(x'^2+y'^2\right)}{4D\tau}} \int dz' \left[z' e^{\frac{-z'^2}{4D\tau}} \int dt \left[\frac{1}{(4\pi D t)^{5/2}} e^{\frac{-\left((x-x')^2+(y-y')^2+z'^2\right)}{4Dt}}\right]\right]\right]\right]$$

(S11)

We can solve the time average integral as:

$$h(x-x',y-y',z') = \int dt \left[\frac{1}{(4\pi D t)^{5/2}} e^{\frac{-\left((x-x')^2+(y-y')^2+z'^2\right)}{4Dt}} \right] = \frac{1}{2\pi^2 D} \frac{1}{\left((x-x')^2+(y-y')^2+z'^2\right)^{3/2}}$$

(S12)

Equation S12 shows that the h goes as $1/\rho^3$ for $\rho = \sqrt{(x-x')^2+(y-y')^2} \gg z'$. This functional form becomes the form factor for remaining integrals, and it explains why the final return distribution scales as $1/\rho^3$.

From here on, we ignore some constants and pre-factors, and rely on the fact that the distribution function must be normalized at the end. Using equation S12, we re-write equation S11 as:

$$f_{tot}(x,y) = N \int dx' \left[\int dy' \left[e^{\frac{-\left(x'^2+y'^2\right)}{4D\tau}} \int dz' \left[z' e^{\frac{-z'^2}{4D\tau}} h(x-x',y-y',z') \right] \right] \right]$$

(S13)

Where N is the normalization factor. We define the z' integral as:

$$g(x-x',y-y') = \int dz' \left[z' e^{\frac{-z'^2}{4D\tau}} h(x-x',y-y',z') \right]$$

(S14)

To continue, we estimate this function. For this, we realize the important feature is the functional form given by h, and think of it as weighted against a distribution $z' e^{\frac{-z'^2}{4D\tau}}$. Borrowing ideas from heavy tailed distribution, we use "typical value" or the mode of the weighting distribution. The mode is given by: $z' = \sqrt{2Dt}$. Up to some prefactor (buried into the normalization constant in eq. S13), we can estimate g as:

$$g(x-x',y-y') \sim \frac{1}{\left((x-x')^2+(y-y')^2+2D\tau\right)^{3/2}}$$

(S15)

Finally, we can compute the return displacement distribution as:

$$f_{tot}(x,y) = N \int dx' \left[\int dy' \left[e^{\frac{-\left(x'^2+y'^2\right)}{4D\tau}} h(x-x',y-y') \right] \right] = N \left[e^{\frac{-\left(x'^2+y'^2\right)}{4D\tau}} \otimes^{(2)} g(x',y') \right]$$

(S16)

Where $\otimes^{(2)}$ is the 2-D convolution.

In figure S4a, we show the results of a simulation versus the computed return displacement distribution. The agreement is good with some error arising from the estimate we force in equation S15. In figure S4b, we show the long range form of the simulation and the computed return displacement distribution. As discussed in the manuscript and expected from the form in equation S12, the long range behavior decays proportional to $1/\rho^3$. Armed with a good approximation for the return displacement distribution function, we can compute the evolution of the patch flux as described in the manuscript.

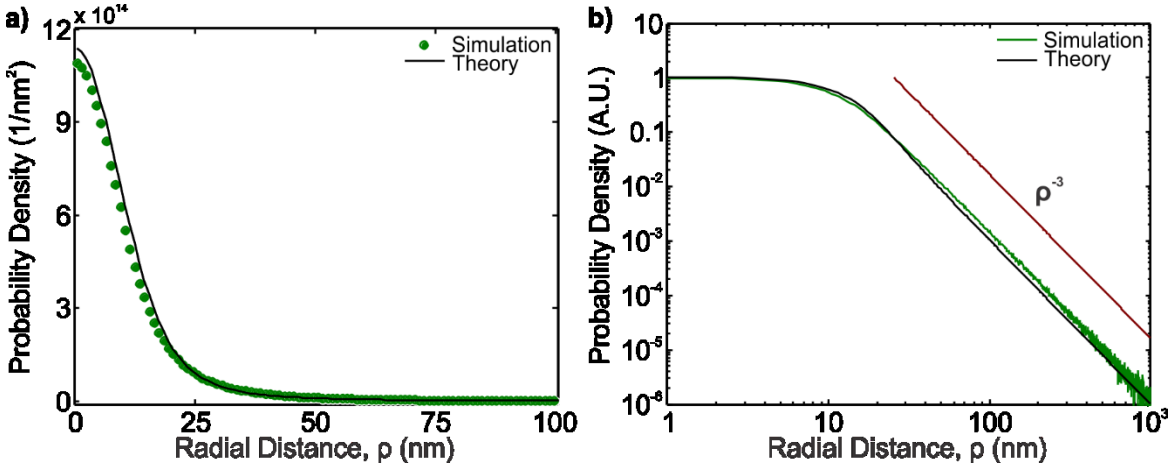

Figure S4. **a)** Plot showing the comparing data extracted from simulation with temporally averaged return displacement distribution function (tRDF) estimated in equation S16. **b)** Simulated and estimated tRDF for large displacement (ρ). As expected from equation S12, the long range distribution scales as $1/\rho^3$. The red line shows a curve proportional to $1/\rho^3$ for comparison.

In figure S5, we show how change the MFP alters the profile. We observe the profiles become sharper, but still maintain the $1/\rho^3$ behavior. Moreover, we note the long range behavior starts to become apparent at radial distance greater than the 2D MFP (here $\sqrt{4D\tau}$).

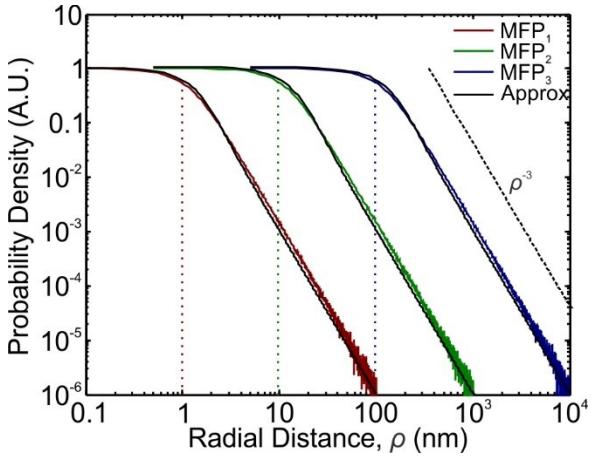

Figure S5. Log-log plots of the relative tRDF for different mean free path values (MFP_1 = 1.2 nm, MFP_2 = 12 nm, MFP_3 = 120 nm) . The colored lines are extracted from Monte Carlo simulations, while the solid black lines represent the respective approximations from equation S16. The black dashed line is a guide for seeing the long range distribution scales ~ρ^{-3}. The colored dashed lines are the approximate scaled lateral MFP. It is clear from the graph that the curves all have a knee at the lateral MFP. This provides the intuition as to where on average the particles will return to the surface: beyond the lateral MFP, it scales as ρ^{-3}, but below that, it scales differently.

Calculation of C_{Bulk}^{eff}

In the manuscript, we discuss the need to rescale the bulk concentration to an effective bulk concentration to account for the fact that we work with simulation with a finite system not an infinite one. Figure S5 shows a cross section of the concentration profile for the infinite system. Our simulations are set in a 10 x 10 x 10 μm^3 box, (cross section show as the black lines in figure S5). To calculate C_{Bulk}^{eff}, we compute the number of particles in our simulation box as:

$$N_V = \iiint dV[c(x,y,z)] \tag{S17}$$

Where N_V is the average number of particles expected in our simulation box for the infinite case, V is the box volume we integrate over, and $c(x,y,z)$ is the concentration profile for the infinite case.

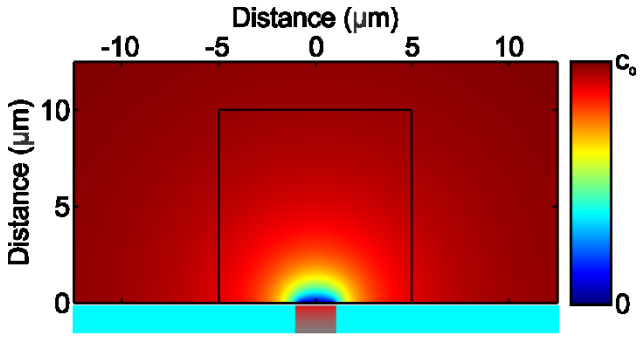

Figure S5. Image showing a cross-section of the concentration profile for an infinite system. The cross section of our simulation box is outlined.

Next we compute the ratio of the number particles in a box filled with the bulk concentration, c_o and the average number of particles expected in our simulation box:

$$r = \frac{c_o V}{N_V} \approx 0.91 \tag{S18}$$

We assume that our simulation acts fairly close to the infinite case, and calculate C_{Bulk}^{eff} as:

$$C_{Bulk}^{eff} = \frac{r N_V^{(s)}}{V} \tag{S19}$$

Where $N_V^{(s)}$ is the number of particles we place in our box.

References:

(1) Carroll, K. M.; Wolf, H.; Knoll, A.; Curtis, J. E.; Zhang, Y.; Marder, S. R.; Riedo, E.; Duerig, U. Understanding How Charged Nanoparticles Electrostatically Assemble and Distribute in 1-D. *Langmuir* **2016**, *32*, 13600–13610.