**Supplementary Information**

**Manipulation and Statistical Analysis of the Fluid Flow of Polymer Semiconductor Solutions during Meniscus-Guided Coating**

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**Fluid strain rate**

The velocity *~v* at any given position in the fluid can be written as a row vector: [*u v w*]. The del operator ∇ is the column vector . We define **J** to be the Jacobian of the velocity, which can be written as the matrix of partial derivatives of the component-wise velocities. **J** is equivalent to the matrix representation of the dyadic tensor :

, (1)

where is shorthand for . is called the velocity gradient and can be split into its symmetric part **E** and anti-symmetric parts **R**:

(2)

(3)

, (4)

where **E** is called the rate-of-strain tensor, and **R** is the vorticity tensor. **E** captures the shear strain imposed upon a control volume of fluid that causes deformation, whereas **R** is a traceless tensor that describes (shearless) rotation of the fluid. For our purposes, we only focus on the components of **E**, which can be written in matrix notation as:

. (5)

For a general fluid, the second-rank stress tensor **T** can be thought of as encapsulating the state of stress on a given control volume of fluid. This quantity appears in Cauchy’s equation of motion but does not have a direct functional relationship to other known variables in the governing equations for fluid flow. We must develop “constitutive” equations to establish such a relationship. We assume that **T** is related to some function *τ* of the velocity gradient and higher order spatial derivatives:

, (6)

where *p* is the pressure, and **I** is the identity tensor. It can be shown that *τ* depends explicitly on the rate-of-strain tensor **E** and not on the vorticity tensor **R**.15 For Newtonian fluids, we assume that *τ* is linear in **E**:

,(7)

where **A** = *Aijkl* is a fourth-order tensor (acting as the proportionality constant). We can assume that the constitutive equation for the fluid is unchanged by coordinate system rotations (i.e., that the fluid is isotropic) and thus impose a general functional form of **A** that involves three arbitrary scalar constants λ, µ, and *ν* (additional details can be found in Reference 15). Because of the symmetry of **E**, *ν* = 0 and we have

.(8)

This is the general constitutive equation for Newtonian fluids. If the fluid is incompressible, , and equation 8 becomes

,(9)

where µis called the shear viscosity. In the general case, both λ and µare involved in the bulk viscosity.

Each of the diagonal terms of the matrix representation of **E** (*ex*, *ey*, and *ez*) describes the extensionalstrain rate for their respective directions, while the off-diagonal elements represent the shear strain rates.

**The second invariant and a tensor norm**

With **E**, we can quantitatively compare the locally imposed shear strain in any region of the simulation box. However, it is desirable to transform **E** into a scalar quantity to facilitate a comparison across simulations. A set of commonly used scalar values to describe a general strain tensor is derived from the calculation of the principal strains on a control volume. For a volume experiencing strain, it is intuitive that the tensor describing the strain should be independent of the coordinate axes defined, and yet **E** is dependent on the coordinate system. The notation of “principal strains” describes the strain independent of any coordinate transformation and is described using the eigenvalues λ(the principal values) and eigenvectors (the principal vectors) of the matrix representation of **E**:

. (10)

Expanded, this becomes: , where are the principal invariants of the

rate-of-strain tensor:

(11)

(12)

. (13)

Note that in the incompressible case . The second invariant is precisely related to the deviatoric part of the strain and can be used to calculate an effective overall strain rate .16 When expanded as a function of the spatial derivatives of the velocity components, equals:

(14)

. (15)

We define the effective strain rate as:

(16)

Given that the components of can be negative, we also wish to use a metric that effectively ignores sign and instead compares the magnitude of the values across our simulations, which define coordinate axes at the same position in each case. Furthermore, we wish to weight each tensor element of **E** equally since we are interested in the strain rate occurring in any direction. This makes intuitive sense in the case of determining the influence of strain on flow-induced polymer nucleation in solution, where the direction of the strain may not matter as much as the magnitude of the resulting strain rate.

With these two conditions, we identify the Frobenius matrix norm (Euclidean norm) of the tensor **E** (when written as a matrix) as a useful metric. The Frobenius norm can be thought of as an extension of the familiar Euclidean vector norm (the 2-norm, or *l*2-norm) to each of the matrix elements and is defined as:

, (17)

where are the matrix elements of **M**. This norm also provides an easy scalar value with which comparisons across simulations can be made, and we refer to norm of the matrix representation of the rate-of-strain tensor as . Note that all usages of the refer to the Frobenius norm regardless of subscript.

**Simulation boundary conditions and parameters**

In the COMSOL software package, we are interested in the steady-state fluid velocity profile from which we can calculate the strain rate tensor **E**at any mesh element. We place our simulation box at the trailing edge of the coating blade and not beyond it (**Figure 1**). The difficulty in modeling fluid dynamical phenomena in the meniscus region has been previously discussed, so we restrict our models to the region under the coating blade. In this way, we can ignore the complex phenomena related to solution viscosification, solvent evaporation, and interfacial flows among others while evaluating the effect of upstream fluid flow before the meniscus. The boundary conditions that approximate the real experimental conditions are chosen to maximize the predictive accuracy of the simulations. The inlet to the simulation box is a plane at *x* = 9*b* and is modeled as a so-called “open boundary” (or a stress-free boundary), which corresponds with the case where the fluid interface is in contact with a larger body of fluid (see **Table S1**). A periodic boundary condition is chosen at the sides of the box (planes *x* = 0 and *x* = *a*) because the pillar array has translational symmetry and because we are not interested in edge effects. We choose the fluid outlet to be a zero-pressure-difference boundary with suppressed backflow because we expect no substantial pressure difference across this plane (at *y* = 0). In principle, there may be substantial back pressures coming from the meniscus region, but these more complex effects are difficult to simulate. Lastly, we assume the standard no-slip condition for all solid-liquid interfaces.

When evaluating the effect of pillar geometry, we use a “parametric sweep” to automatically generate and compute the finite element mesh for a variety of pillar arrays. Since the arrays are 2D lattices (rectangular Bravais lattices), we name them as ordered pairs (*a*,*b*) of their interpillar distance *a* within a row (*x*-direction) and inter-row distance *b* (*y*-direction) in units of µm. The lattice constants for the unit cell of the pillar array would be and . The last parameter varied is the coating speed, which we input as the negative *y*-velocity of the bottom substrate boundary. This is equivalent to modeling the movement of the coating blade in the positive *y*-direction and merely uses the blade’s frame of reference.

Representative values and parameters resulting from the simulations for each of the arrays are shown in **Table S2** for reference.

|  |  |
| --- | --- |
| **COMSOL Boundary Condition** | **Equation** |
| No-slip boundary |  |
| Open boundary |  |
| Pressure boundary | , where |
| Periodic boundary | , where |

**Table S1. Equations used in COMSOL for simulation boundary conditions.**

Here, is the fluid velocity vector, µis the fluid viscosity, is the unit vector normal to the boundary, is the specified boundary pressure, is the calculated boundary pressure, is the boundary pressure difference, and *src* and *dst* refer to the source and destination, respectively.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Array** | | **Results** | | | | | | | | **Simulation Parameters** | | |  |
| **Outlet** | | | | | **Slanted** | | |
| *a*  (µm) | *b*  (µm) | Average Norm | Average Strain Rate | Average Velocity | Volumetric Flow Rate | Flux |  |  | Flux | Deg. of Freedom | Relative  Error | Iter. | Sim.  Time  (s) |
| 50 | 30 | 0.45 | 0.52 | 0.40 | 0.33 | 0.40 | 0.45 | 0.38 | 0.45 | 366012 | 2*.*3 × 10−13 | 4 | 200 |
| 50 | 40 | 0.49 | 0.45 | 0.50 | 0.40 | 0.50 | 0.56 | 0.51 | 0.56 | 386640 | 7*.*1 × 10−13 | 4 | 204 |
| 50 | 50 | 0.53 | 0.48 | 0.58 | 0.47 | 0.58 | 0.56 | 0.53 | 0.56 | 391516 | 2*.*3 × 10−13 | 4 | 206 |
| 50 | 60 | 0.55 | 0.54 | 0.61 | 0.49 | 0.61 | 0.63 | 0.62 | 0.63 | 385328 | 7*.*6 × 10−13 | 4 | 193 |
| 50 | 70 | 0.69 | 0.76 | 0.73 | 0.59 | 0.73 | 0.59 | 0.59 | 0.59 | 385628 | 3*.*9 × 10−13 | 4 | 193 |
| 50 | 80 | 0.98 | 0.88 | 1 | 0.80 | 1 | 0.82 | 0.82 | 0.82 | 382620 | 1*.*4 × 10−12 | 4 | 179 |
| 50 | 90 | 1 | 0.80 | 0.99 | 0.80 | 0.99 | 1 | 1 | 1 | 366140 | 8*.*6 × 10−13 | 4 | 168 |
| 50 | 100 | 0.76 | 1 | 0.79 | 0.64 | 0.79 | 0.79 | 0.82 | 0.79 | 353960 | 2*.*2 × 10−12 | 4 | 167 |
| 60 | 50 | 0.57 | 0.64 | 0.60 | 0.58 | 0.60 | 0.51 | 0.49 | 0.51 | 387672 | 2*.*9 × 10−13 | 4 | 225 |
| 70 | 50 | 0.62 | 0.56 | 0.64 | 0.72 | 0.64 | 0.54 | 0.53 | 0.54 | 391324 | 2*.*1 × 10−13 | 4 | 215 |
| 70 | 70 | 0.70 | 0.68 | 0.73 | 0.82 | 0.73 | 0.53 | 0.54 | 0.53 | 396228 | 4*.*8 × 10−13 | 4 | 248 |
| 80 | 50 | 0.56 | 0.60 | 0.59 | 0.75 | 0.59 | 0.50 | 0.50 | 0.50 | 395832 | 1*.*9 × 10−13 | 4 | 217 |
| 90 | 50 | 0.54 | 0.54 | 0.57 | 0.83 | 0.57 | 0.47 | 0.48 | 0.47 | 388732 | 1*.*3 × 10−13 | 4 | 214 |
| 100 | 50 | 0.59 | 0.56 | 0.62 | 1 | 0.62 | 0.49 | 0.50 | 0.49 | 389300 | 4*.*5 × 10−14 | 4 | 215 |
| Max | | 53 | 52 | 0*.*68 | 8*.*8×105 | 676 | 0*.*080 | 5*.*0×105 | 80 |  | | |  |

**Table S2. Representative values and parameters resulting from the simulations for each of the arrays.**

Normalized values for the average Frobenius tensor norm , average strain rate , average fluid velocity , and volumetric flow rate , and flux on two boundaries: the outlet plane and the slanted entry plane into the pillar array (the plane incident with the ends of the pillars inclined at 8°). The last row indicates the value corresponding to the normalized value of 1 for each result column. Simulation parameters, including the degrees of freedom, relative error, number of iterations, and overall simulation time for each of the pillar arrays analyzed, are also shown.

# **Statistical analysis**

In this article, we seek to determine whether some correlation exists between our set of 130 predictors (**Table S3**) and three metrics with implications for device performance: the relative degree of crystallinity in the final dry thin-film and the charge-carrier mobilityof bottom-gate, top-contact thin-film transistors, where the charge transport direction is parallel and perpendicular to the coating direction. Given we do not have an *a-priori* model linking such variables, we use a simple linear correlation so as to not impose a functional bias on analysis, and because we are interested in observing statistical correlations rather than developing rigorous predictive models, linear correlation is sufficient. In this context, the correlation coefficient (the Pearson correlation coefficient) serves as a proxy for the strength of the linear correlation, while the *p*-value is a measure of the probability that the data exhibits a non-negligible linear relationship between response variable and predictor. The null hypothesis is that , or in other words, that there is no relationship between response and predictor as defined by .

Conventional wisdom has asserted statistical significance when a *p*-value is less than 0*.*05, but recent issues with the reproducibility of published findings have drawn calls for more statistically rigorous analyses of data. In this article, we are interested in revealing potential predictors of macroscopic performance metrics in an effort to guide future research, and thus we use only as the threshold for statistical suggestivenessand report the upper bound of the Bayes factor to provide additional context. The Bayes factor bound (BFB) is defined as

, (18)

where *p* is the *p*-value for a calculated value of ,and is the mathematical constant.30 We believe this analysis is sufficient for the purpose of guiding additional research into the predictors discussed here and of revealing the possible importance of variables influencing macroscopically observable variables such as rDoC and field-effect mobilities.

Each of the 6 tensor elements and their 15 pairwise multiplicative interactions are calculated for four different sub-regions of the simulation box (**Table S4**) in addition to the entire volume. This binning of values allows us to calculate the values without averaging over large volumes of the simulation space that do not exhibit phenomena of interest. We note that further effort to identify and optimize the binning volumes can lead to stronger indications of which predictors exhibit real linear correlations with response variables of interest.

|  |  |  |
| --- | --- | --- |
| **Variable** | | **Units** |
| *a* | |  |
| *b* | |  |
| *a*:*b* ratio | | — |
| Outlet area | |  |
| Outlet-averaged strain tensor norm and strain rate | |  |
| Outlet-averaged velocity | |  |
| and | |  |
| Max velocity | |  |
| Outlet volumetric flow rate | |  |
| Outlet flux | |  |
| Slanted-plane average velocity | |  |
| Slanted plane area | |  |
| Slanted-plane volumetric flow rate | |  |
| Slanted-plane flux | |  |
| Outlet-volume-averaged and | |  |
| First-row-volume-averaged and | |  |
| First-row-plane-averaged and | |  |
| Outlet-volume-averaged velocity | |  |
| First-row-volume-averaged velocity | |  |
| Row-plane-averaged velocity | |  |
| The 6 unique rate-of-strain tensor elements and their 15 interactions: averaged in the (1) outlet plane, (2) outlet volume,  (3) first-row volume, and  (4) first-row pillar plane, along with the (5) maximum values in the simulation volume. |  |  |
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**Table S3. List of predictors.**

|  |  |  |
| --- | --- | --- |
| **Binning Region** | **Description** | **Numerical Description** |
| Outlet plane | The outlet boundary, an *x*-*z* plane |  |
| Outlet volume | The volume close to the outlet | The volume between the planes and |
| First-row volume | The volume  surrounding the first row of pillars | The volume between the planes and |
| First-row (pillar) plane | The tilted plane parallel with the long axis of the pillars midway between the last pillar row and the  outlet | The plane uniquely specified by the points |
| Slanted plane | The tilted plane touching the bottom of all of the pillars | All points where and |

**Table S4. Description of the binning regions used for the statistical analysis.**

The slanted plane was used primarily to calculate the fluid flux into the pillar array. is the height of the pillars (20 µm), is the blade tilt angle (8°), is the inter-pillar distance, is the inter-row distance, and is the outer radius of the crescent (17*.*5 µm). Note that for the first pillar row, the centers of the crescents are offset from the outlet, and each subsequent row is offset by .

# **Supplementary data**

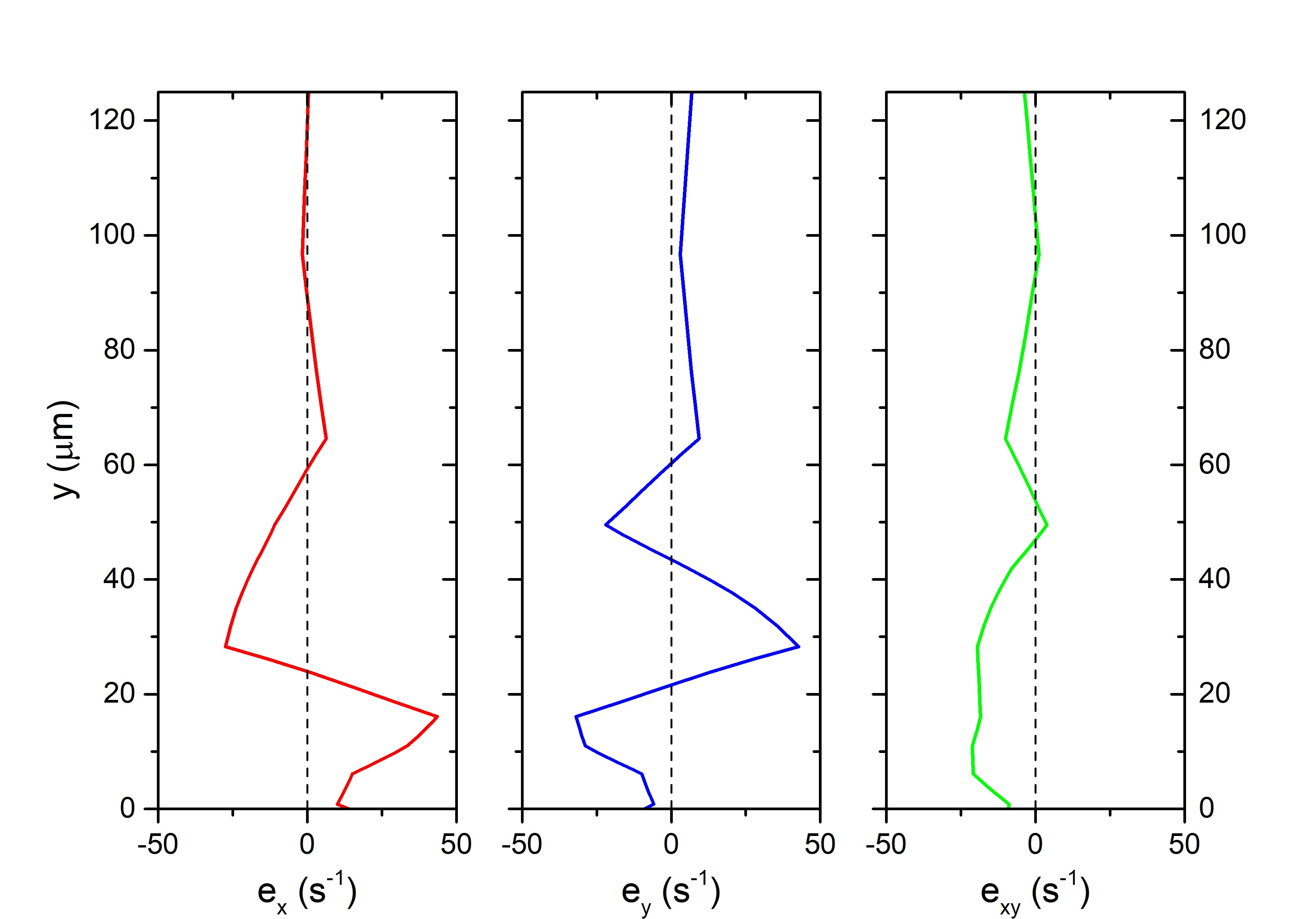


Figure S1. Vertical plots of *ex* (red), *ey* (blue), and *exy* (green) along a streamline from the (50,30) array simulation originating at (*x, y, z*) = (40*,* 125*,* −15) µm. The outlet is at *y* = 0, and the overall fluid flow direction is in the negative *y*-direction (downward). Zero strain is shown as a vertical dashed line in each plot.

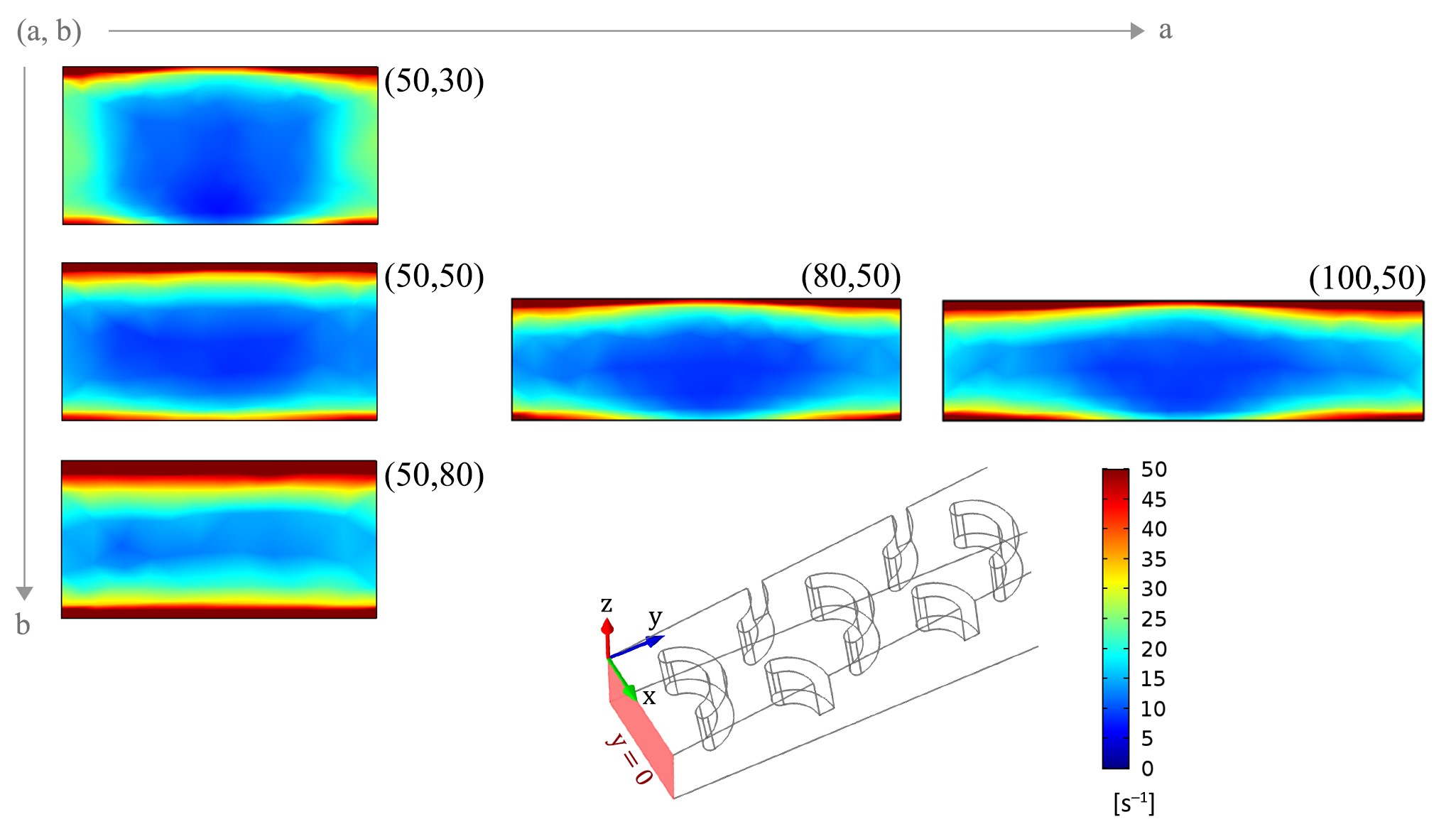


Figure S2. Rate-of-strain Frobenius tensor norm on the *y* = 0 outlet cut-plane for a selection of pillar arrays during coating at .

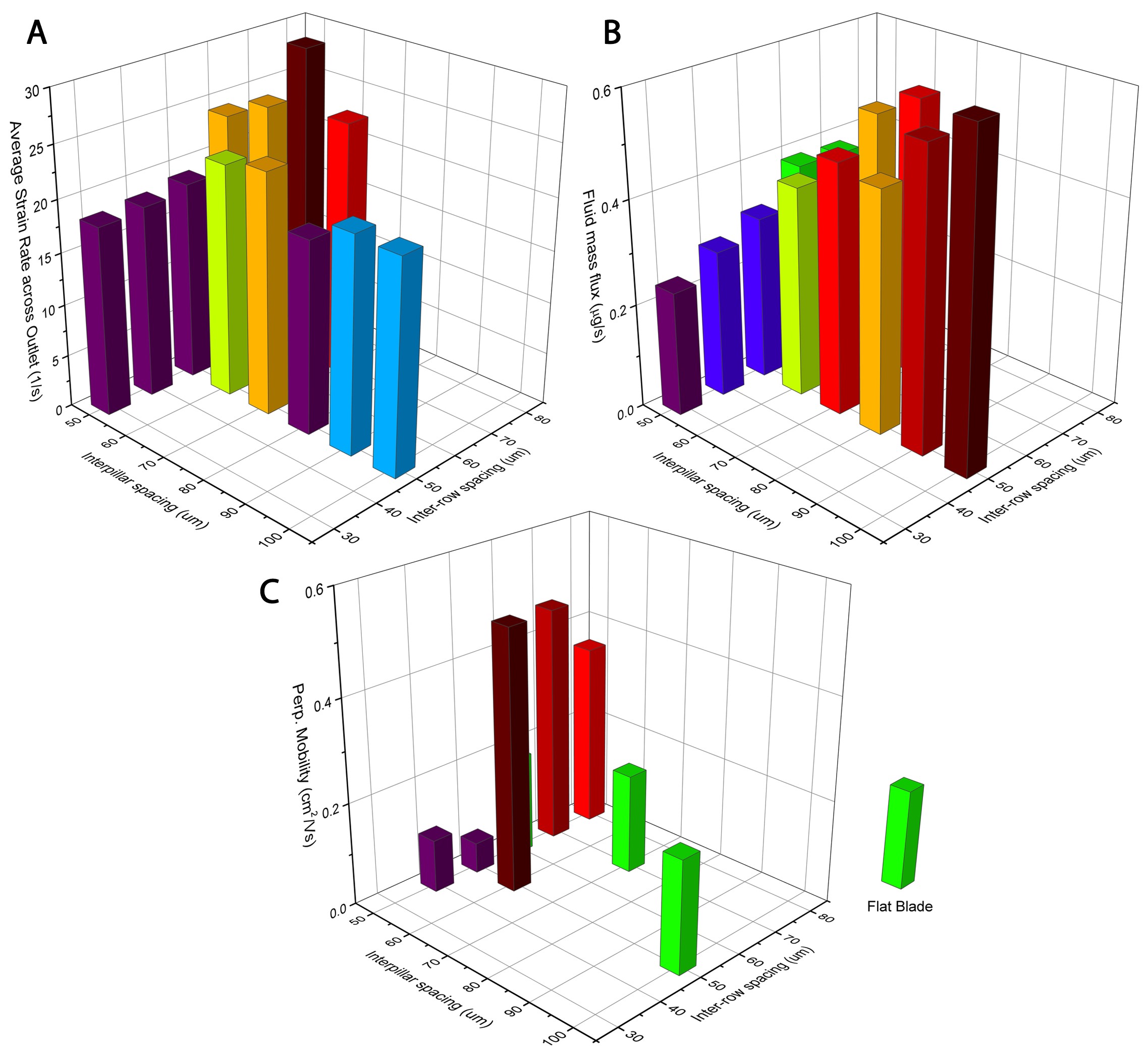


Figure S3. (a) The area-averaged strain rate Frobenius tensor norm across the outlet during coating with crescent pillar arrays does not follow the trend of the previous plots. Higher *b* appears to yield modestly higher . (b) Mass flux of the simulated fluid (density *ρ* = 0*.*878 g mL−1) crossing the slanted entry plane into the pillar array (the plane incident with the ends of the pillars inclined at 8°). Note that for small inter-pillar *a* and inter-row *b*, there is reduced fluid flow into the regions between the pillars. (c) Perpendicular field-effect hole mobilities µperp of polymer films deposited by patterned coating blades of various pillar spacings, where the charge transport direction is transverse to the coating direction.

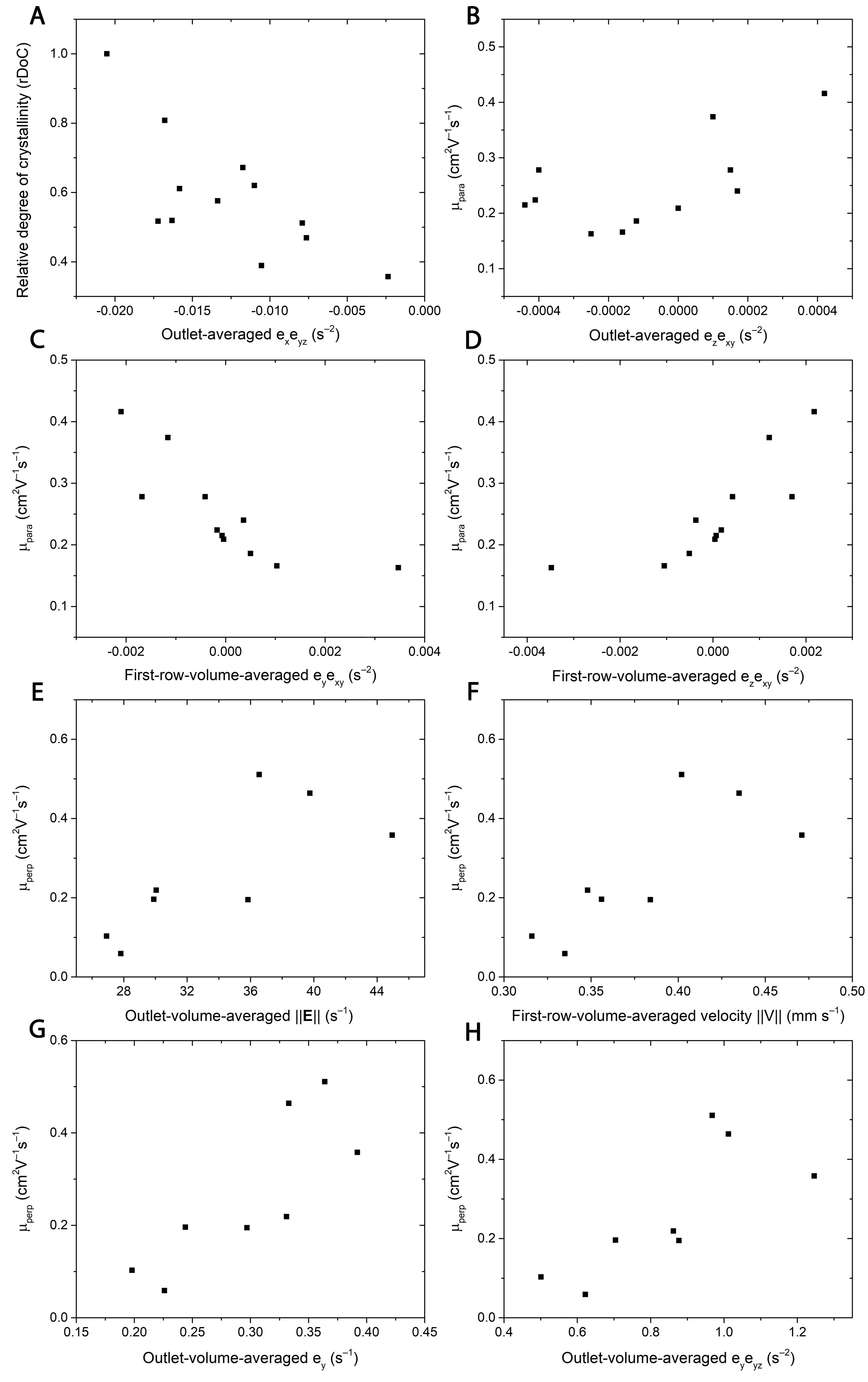


Figure S4. Relative degree of crystallinity as a function of (a) the tensor element *exeyz* averaged over the outlet plane. Parallel charge carrier mobility *µ*para as a function of (b) *ezexy* averaged over the outlet plane, (c) *eyexy*, and (d) *ezexy* each averaged over the solution volume surrounding the first row of pillars. Perpendicular charge-carrier mobility µperp as a function of (e) the rate-of-strain Frobenius tensor norm averaged over the solution volume near the outlet, (f) the fluid velocity *V* averaged over the solution volume surrounding the first row of pillars, and (g) *ey* and (h) *eyeyz* both averaged over the solution volume near the outlet.

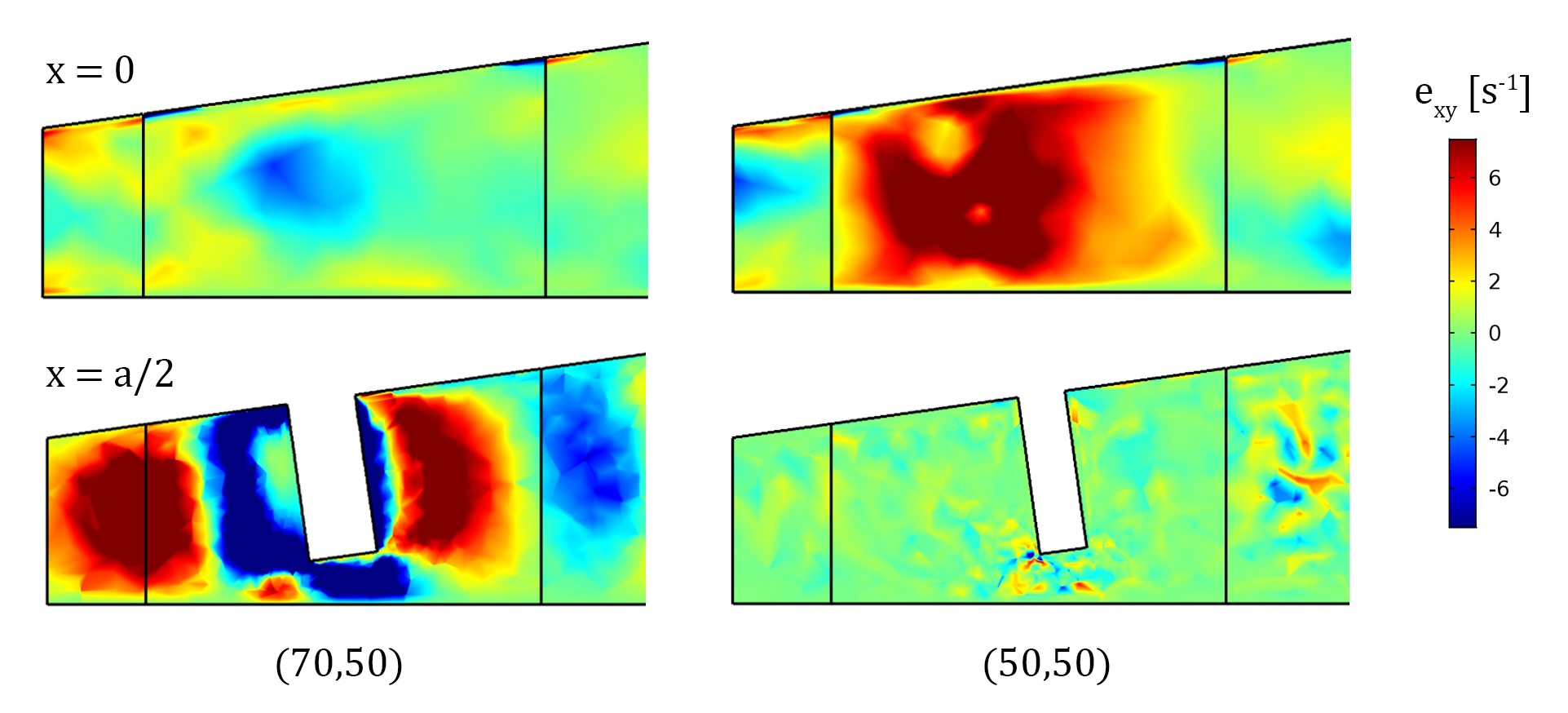


Figure S5. Cross-sections consisting of *y*-*z* planes at (top) and (bottom) for the (70,50) (left) and (50,50) (right) arrays shaded by the value of *exy* at each position. Within each image, the solid vertical lines demarcate the outlet volume (left) and the first-row volume (center).

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Dependent Variable** | **Predictor** | **Lower Bound** | ***R*** | **Upper Bound** |
| Relative degree of crystallinity | Outlet-averaged *ex* | −0*.*89 | −0*.*66 | −0*.*13 |
| Outlet-averaged *exeyz* | −0*.*92 | −0*.*73 | −0*.*26 |
| Parallel mobility | Outlet-averaged *ezexy* | 0*.*034 | 0*.*62 | 0*.*89 |
| First-row volume-averaged *exy* | −0*.*95 | −0*.*82 | −0*.*42 |
| First-row volume-averaged *eyexy* | −0*.*94 | −0*.*79 | −0*.*37 |
|  | First-row volume-averaged *ezexy* | 0*.*38 | 0*.*80 | 0*.*95 |
|  | First-row volume-averaged *exyeyz* | −0*.*91 | −0*.*68 | −0*.*13 |
| Perpendicular mobility | Outlet-volume-averaged  First-row volume-averaged velocity *V*  Outlet-volume-averaged *ey* | 0*.*11 0*.*16  0*.*27 | 0*.*76 0*.*78  0*.*82 | 0*.*95 0*.*96  0*.*97 |
| Outlet-volume-averaged *eyeyz* | 0*.*13 | 0*.*77 | 0*.*96 |

**Table S5. 95% confidence interval bounds of *R* for each of the predictors that are at least statistically suggestive.**

|  |  |  |
| --- | --- | --- |
| ***a* (µm)** | ***b* (µm)** | **Thickness (nm)** |
| 50 | 30 | 139 |
| 50 | 40 | 139 |
| 50 | 50 | 147 |
| 50 | 60 | 241 |
| 50 | 70 | 149 |
| 50 | 80 | 124 |
| 60 | 50 | 213 |
| 70 | 50 | 107 |
| 70 | 70 | 161 |
| 80 | 50 | 124 |
| 90 | 50 | 118 |
| 100 | 50 | 130 |

**Table S6. Film thicknesses of deposited PDPP3T thin-films.**

There is relatively little variation among the films, which average 149 nm.