Evaporation-induced self-assembly of diblock copolymer films in an electric field: a simulation study

Oliver Dreyer,[†] Ludwig Schneider,[‡,¶] Maryam Radjabian,[†] Volker Abetz,[*,†,§] and Marcus Müller[*,‡]

[†]*Helmholtz-Zentrum Hereon, Institut für Membranforschung, Max-Planck-Straße 1,*
21502 Geesthacht, Germany

[‡]*Georg-August Universität Göttingen, Institut für Theoretische Physik,*
Friedrich-Hund Platz 1, 37077 Göttingen, Germany

[¶]*Pritzker School of Molecular Engineering, University of Chicago, 5640 South Ellis Avenue,*
Chicago, IL 60637 , USA

[§]*Universität Hamburg, Institut für Physikalische Chemie, Martin-Luther-King Platz 6,*
20146 Hamburg, Germany

E-mail: volker.abetz@hereon.de; mmueller@theorie.physik.uni-goettingen.de

Supporting Information

Using Convolution to Calculate the Electric Potential Field

In order to show that convolution does not significantly interfere with the resulting morphology, several validation simulations were conducted. These validation simulations were simple solvent-evaporation tests with a diblock copolymer composition A_9B_{23} and $\chi_{SG}N_0 = 0$. The remaining parameters can be found in Table 1. In contrast to our typical simulations, the initial state was set to be shortly after the emergence of perpendicular A cylinders. We employed this very same starting configuration for all validation simulations presented in the following. In combination with choosing the same random number generator (RNG) seed, the best possible comparison is established. Validation simulations have been run for 5000 Monte-Carlo steps (MCS) and the final variance of the density field has been examined, focusing on the emerging structure to rule out possible systematic shifts due to convolution.

To create a baseline of how strongly different systems deviate under these conditions, simulations have been performed for the following cases: without application of an electric field, utilizing the same and different RNG seed, different field strengths, calculated with and without convolution, varying between $0.03\,\mathcal{E} \leq E_0 \leq 0.06\,\mathcal{E}$, and exhibiting a microscopic change to the initial state. The latter was achieved by letting the original state propagate for 100 MCS and using the output as the updated initial configuration, ensuring the same RNG seed. After roughly 2000 MCS, the average density deviation between these simulations settles around 16% in all cases, mainly due to the chaotic behavior of the microscopic degrees of freedom. Consequently, the variation in the density observed by comparing the calculation of the electric field with and without convolution is within the tolerable range.

To eliminate the possibility for a systematic divergence on the polymer density within the area appropriate for phase separation caused by the convolution method, a total of four simulations are compared. On the one hand, the density difference for a simulation where the electric field was calculated with and without convolution is examined. Additionally, the procedure is repeated but with a microscopic change to the initial state of the simulation. Thus, two density field difference plots are obtained that can be used, once again, to calculate their difference, highlighting if distinct effects are observed due convolution. Figure S1 displays the density field cross-section of (a) the minority block in the liquid phase and (b) the resulting difference of the density difference fields. A small density deviation is observed within the homogeneous solution in the deeper parts, $z \geq 30\Delta L$, with $\Delta L = R_{\mathrm{e}}/10$. On the other hand, stronger fluctuations are noticeable within the already established cylindrical microphases which, however, appear distributed randomly giving no indication of a systematic effect due to convolution.

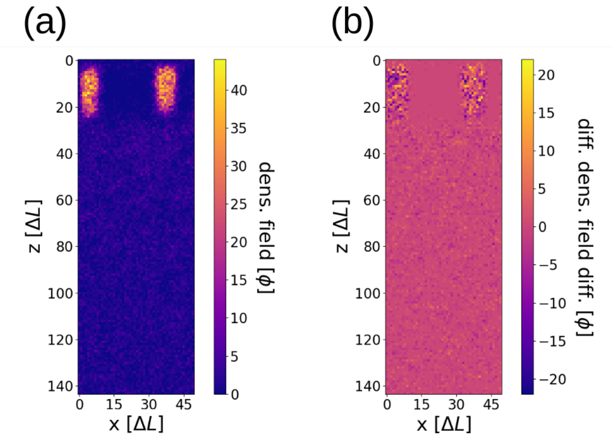

Figure S1: Cross-sections of the simulation box. Only the liquid phase is shown. (a) displays the minority block density and (b) displays the difference of the density-field differences in absolute values.

Model and simulation scheme

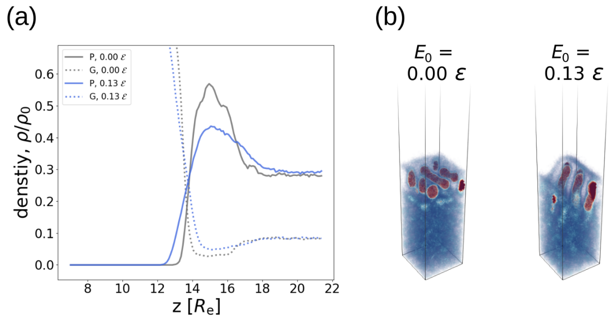

Figure S2: Effect of a high electric field strength on the film surface for a system of Table 1 with $\chi_{\mathrm{SG}}N_0 = 30$, resulting in low evaporation rates. (a) 1D density profile with and without electric field applied, (b) respective simulation snapshots at $t = 50.2\ \tau_{\mathrm{R}}$. Due to an electric field, $E_0 = 0.13\ \mathcal{E}$, the film surface roughens and appears broadened along the z axis in the 1D profile. The simulation snapshots highlight that an electric field is able to realign the cylindrical microphases of the minority block, however, the roughening of the film surface allows for locally higher evaporation rates. In our simulations, solvent selectivity is tuned by adjusting a repulsive interaction between solvent and minority block, $\chi_{\mathrm{AS}}N_0 = 20$, while having a favorable interaction with the majority block, $\chi_{\mathrm{BS}}N_0 = 0$.

Cylinder Alignment by an Electric Field

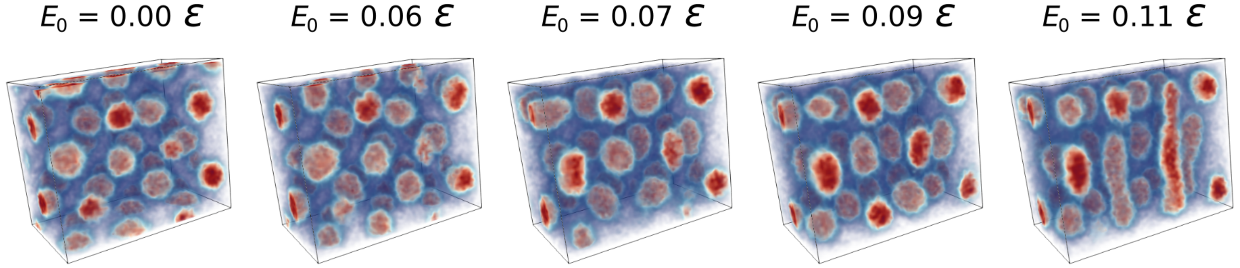

Figure S3: Effect of varying electric-field strength on a spherical morphology of the minority block. The simulations feature bulk polymer solutions of an A_7B_{25} diblock copolymer with a density $\phi_{\mathrm{P}} = 0.77$ without solvent evaporation. The remaining parameters for the respective system are listed in Table 1. In these simulations, microphase separation initially occurred in the absence of an electric field. Then, the electric field was turned on, and subsequently the structure evolved under the influence of an electric field for a duration of 6 τ_{R}. The electric field distorts the spheres to ellipsoids. This effect becomes clearly visible around $E_0 \geq 0.07\ \mathcal{E}$. Eventually, at $E_0 = 0.11\ \mathcal{E}$, ellipsoids connect and form cylinders. We emphasize, that this order-order transition (OOT) differs from the evaporation simulations in this work, where cylinders form from a single layer of spheres that gradually grow in the course of solvent evaporation within an electric field.

Increased Cylinder Growth in an Electric Field

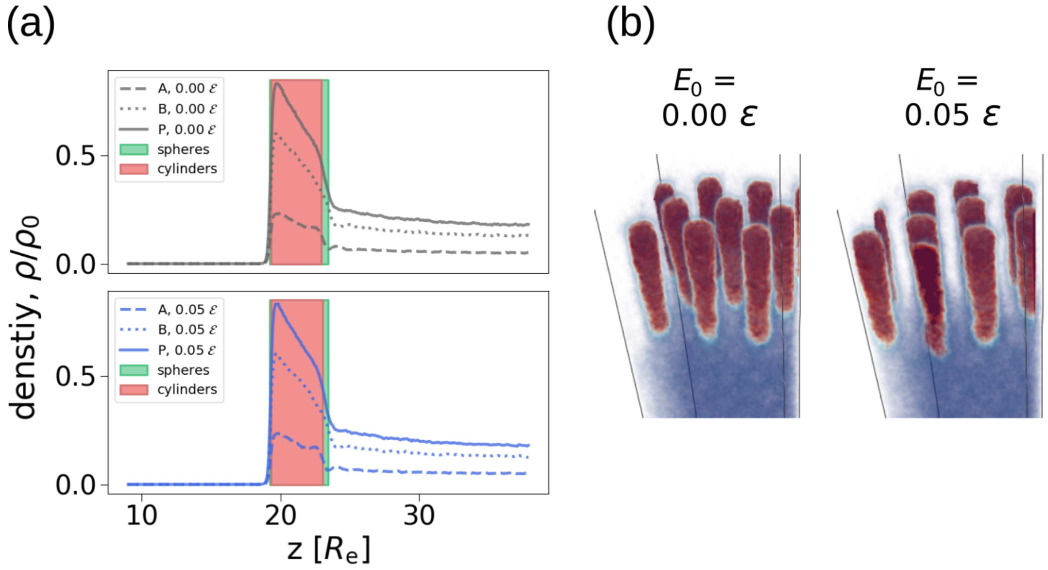

Figure S4: (a) 1D density profiles of solvent evaporation simulations for an unfitting system ($\mathrm{A_9B_{32}}$ in Table 1 with $\chi_{SG}N_0 = 0$) showing the marginal effect of an electric field on the cylindrical layer, l_{cyl} at $t = 26\ \tau_{\mathrm{R}}$. Due to the steep concentration gradient a substantial increase of l_{cyl} is prevented. Gray lines represent the simulation without and blue lines with application of an electric field, $E_0 = 0.05\ \mathcal{E}$. Solid, dashed and dotted lines refer to minority block, A, majority block, B, and the sum of both, P, respectively. Spherical (green) and cylindrical layers (red) are highlighted in both cases. (b) Respective density field snapshots of the two systems.