# Supporting Information: Modeling solvent evaporation during thin film formation in phase separating polymer mixtures 

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## Numerical Methods

We discretize the system of equations in two dimensions and remark that the discretization in three dimensions can be done in a straightforward manner. Let $u_{i}^{n}(j, k)$ be the finite difference grid function evaluated at the $j, k$ node at time step $n$ of the $i$ th variable. Assuming a uniform step in space $\left(h=h_{x}=h_{y}\right)$ and time $(s)$, we discretize in time first semi-implicitly
leading to

$$
\begin{align*}
& \phi_{\mathrm{sl}}^{n+1}-s \nabla \cdot\left(M_{\mathrm{sl}}\left(\left\{\phi_{\alpha}^{n}\right\}\right) \nabla\left(\mu_{\mathrm{sl}}^{n+1}+p^{n+1}\right)\right)-s \stackrel{\circ}{\mathrm{sl}}_{-1} S_{\mathrm{sl}}^{n+1}=\phi_{\mathrm{sl}}^{n}  \tag{S-1}\\
& \phi_{i}^{n+1}-s \nabla \cdot\left(M_{i}\left(\left\{\phi_{\alpha}^{n}\right\}\right) \nabla\left(\mu_{i}^{n+1}+p^{n+1}\right)\right)=\phi_{i}^{n} \text { for } i=p, q  \tag{S-2}\\
& S_{\mathrm{sl}}=-\lambda\left(\stackrel{\circ}{\rho}_{\mathrm{sl}}^{-1} \mu_{\mathrm{sl}}^{n+1}+\left(\stackrel{\circ}{\rho}_{\mathrm{sl}}^{-1}-\stackrel{\circ}{\rho}_{\mathrm{sv}}^{-1}\right) p^{n+1}\right)  \tag{S-3}\\
& \mu_{i}^{n+1}+\epsilon_{i}^{2} \Delta \phi_{i}^{n+1}+\epsilon_{\mathrm{sv}}^{2} \Delta\left(\sum_{j \neq \mathrm{sv}} \phi_{j}^{n+1}\right)=\frac{\partial f_{h}\left(\left\{\phi_{i}^{n}\right\}\right)}{\partial \phi_{i}}  \tag{S-4}\\
& \sum_{i \neq \mathrm{sv}} \nabla \cdot\left(M_{i}\left(\phi_{i}^{n}\right) \nabla \mu_{i}^{n+1}\right)+\sum_{i} \nabla \cdot\left(M_{i}\left(\phi_{i}^{n}\right) \nabla p^{n+1}\right)+\left(\circ_{\mathrm{sv}}^{-1}-\stackrel{\circ}{\mathrm{sll}}_{-1}\right) S_{\mathrm{sl}}^{n+1}=0 . \tag{S-5}
\end{align*}
$$

We discretize in space via the second order central difference scheme and define

$$
\begin{equation*}
\left(\nabla_{h} M_{i} u_{i}\right)\left(j+\frac{1}{2}, k\right)=M_{i}\left(j+\frac{1}{2}, k\right) \frac{u_{i}(j+1, k)-u_{i}(j, k)}{h} \tag{S-6}
\end{equation*}
$$

where

$$
\begin{equation*}
M_{i}\left(j+\frac{1}{2}, k\right)=\frac{1}{2}\left(M_{i}(j, k)+M_{i}(j+1, k)\right) . \tag{S-7}
\end{equation*}
$$

We make similar definitions for $\left(\nabla_{h} M_{i} u_{i}\right)\left(j, k-\frac{1}{2}\right),\left(\nabla_{h} M_{i} u_{i}\right)\left(j, k+\frac{1}{2}\right), \ldots$, and define

$$
\begin{align*}
\left(\nabla_{h} \cdot M_{i} \nabla_{h} u_{i}\right)(j, k) & =\frac{1}{h}\left(\left(\nabla_{h} M_{i} u_{i}\right)\left(j+\frac{1}{2}, k\right)-\left(\nabla_{h} M_{i} u_{i}\right)\left(j-\frac{1}{2}, k\right)\right) \\
& +\frac{1}{h}\left(\left(\nabla_{h} M_{i} u_{i}\right)\left(j, k+\frac{1}{2}\right)-\left(\nabla_{h} M_{i} u_{i}\right)\left(j, k-\frac{1}{2}\right)\right) \\
& =\frac{1}{h^{2}}\left(M_{i}\left(j+\frac{1}{2}, k\right) u_{i}(j+1, k)+M_{i}\left(j-\frac{1}{2}, k\right) u_{i}(j-1, k)\right) \\
& +\frac{1}{h^{2}}\left(M_{i}\left(j, k+\frac{1}{2}\right) u_{i}(j, k+1)+M_{i}\left(j, k-\frac{1}{2}\right) u_{i}(j, k-1)\right) \\
& -\frac{1}{h^{2}}\left(\left(\left(M_{i}\left(j+\frac{1}{2}, k\right)+M_{i}\left(j-\frac{1}{2}, k\right)+M_{i}\left(j, k+\frac{1}{2}\right)+M_{i}\left(j, k-\frac{1}{2}\right)\right) u_{i}(j, k)\right) .\right. \tag{S-8}
\end{align*}
$$

By introducing this discretized operator into the time discretized system we obtain a fully discretized system which results in the large, sparse linear system

$$
\begin{align*}
\phi_{\mathrm{sl}}-s \nabla_{h} \cdot\left(M_{\mathrm{sl}} \nabla_{h}\left(\mu_{\mathrm{sl}}+p\right)\right)-s \rho_{\mathrm{sl}}^{-1} S_{\mathrm{sl}} & =F_{\phi_{\mathrm{sl}}}  \tag{S-9}\\
\phi_{i}-s \nabla_{h} \cdot\left(M_{i} \nabla_{h}\left(\mu_{i}+p\right)\right) & =F_{\phi_{i}} \text { for } i=p, q(\mathrm{~S}-10) \\
S_{\mathrm{sl}}=-\lambda\left(\stackrel{\circ}{\mathrm{sll}}_{\mathrm{sl}}^{-1} \mu_{\mathrm{sl}}+\left(\stackrel{\circ}{\mathrm{sl}}_{-1}^{-1}-\stackrel{\circ}{\mathrm{sv}}_{-1}^{\mathrm{s}}\right) p\right) &  \tag{S-11}\\
\mu_{i}+\epsilon_{i}^{2} \Delta_{h} \phi_{i}+\epsilon_{\mathrm{sl}}^{2} \Delta_{h}\left(\sum_{j \neq \mathrm{sv}} \phi_{j}\right) & =F_{\mu_{i}}  \tag{S-12}\\
\sum_{i \neq \mathrm{sv}} \nabla_{h} \cdot\left(M_{i} \nabla_{h} \mu_{i}\right)+\sum_{i} \nabla_{h} \cdot\left(M_{i} \nabla_{h} p\right)+\left(\stackrel{\circ}{\rho}_{\mathrm{sv}}^{-1}-\stackrel{\circ}{\mathrm{sll}}_{-1}^{1}\right) S_{\mathrm{sl}} & =0 \tag{S-13}
\end{align*}
$$

where the time step has been suppressed. Note that the $M_{i}$ depend on the previous data $\phi_{i}^{n}$, so in this linear system the mobilities $M_{i}$ are spatially dependant but do not depend on the current solution. Similarly, we have introduced the notation $F_{\phi_{i}}, F_{\mu_{i}}$ for the data that depend on the previous time step in (S-1)- (S-5) which comprise the right hand side of the large linear system that we are solving. We solve this system using the Full Approximation Storage (FAS) multigrid method based on the two level algorithm, ${ }^{1]}$ which is extended into an adaptive algorithm as in. ${ }^{[2]}$ For the equations (S-9) - (S-13) we define the solution variables and operators compactly as

$$
\begin{equation*}
\boldsymbol{\Phi}(j, k)=\left(\phi_{s l}(j, k), \mu_{s l}(j, k), \phi_{p}(j, k), \mu_{p}(j, k), \phi_{q}(j, k), \mu_{q}(j, k), p(j, k)\right), \tag{S-14}
\end{equation*}
$$

$\boldsymbol{N}$ the operator on the left hand side, $\boldsymbol{S}$ the right hand side, so that we are solving $\boldsymbol{N}(\boldsymbol{\Phi})=\boldsymbol{S}$. Then for each grid we define $\boldsymbol{\Phi}_{m}, \boldsymbol{N}_{m}, \boldsymbol{S}_{m}$ to be the solution, operator, and right hand side for the $m$ th level grid. The FAS multigrid method is based on the two level method, which
is written as

$$
\begin{aligned}
& \text { Initialize } \boldsymbol{\Phi}_{m}^{0}=\boldsymbol{\Phi}_{m}^{n+1,0} \longleftarrow \boldsymbol{\Phi}_{m}^{n} \text {, the solved solution at the last time step; } \\
& \text { Initialize } \boldsymbol{S}_{m}=\boldsymbol{S}_{m}^{n+1} ; \\
& \text { while }\left\|\boldsymbol{N}_{m}\left(\boldsymbol{\Phi}_{m}^{r}\right)-\boldsymbol{S}_{m}\right\|>\text { tol do } \\
& \quad \begin{array}{l}
\boldsymbol{\Phi}_{m}^{r}=\operatorname{Smooth}^{\lambda}\left(\boldsymbol{\Phi}_{m}^{r}, \boldsymbol{N}_{m}, \boldsymbol{S}_{m}\right) ; \\
\boldsymbol{r}_{m}^{r}=\boldsymbol{S}_{m}-\boldsymbol{N}_{m}\left(\boldsymbol{\Phi}_{m}^{r}\right) ; \\
\text { Restrict } \boldsymbol{r}_{m-1}^{r}=I_{m}^{m-1} \boldsymbol{r}_{m}^{r}, \boldsymbol{\Phi}_{m-1}^{r}=I_{m}^{m-1} \boldsymbol{\Phi}_{m}^{r} ; \\
\text { Solve } \boldsymbol{N}_{m-1}\left(\mathbf{\Psi}_{m-1}^{r}\right)=\boldsymbol{N}_{m-1}\left(\boldsymbol{\Phi}_{m-1}^{r}\right)+\boldsymbol{r}_{m-1}^{r} ; \\
\boldsymbol{e}_{m-1}^{r}=\boldsymbol{\Psi}_{m-1}^{r}-\boldsymbol{\Phi}_{m-1}^{r} ; \\
\operatorname{Prolongate} \boldsymbol{\Phi}_{m}^{r}=\boldsymbol{\Phi}_{m}^{r}+I_{m-1}^{k} \boldsymbol{e}_{m-1}^{r} ; \\
\boldsymbol{\Phi}_{m}^{r}=\operatorname{Smooth}^{\lambda}\left(\boldsymbol{\Phi}_{m}^{r}, \boldsymbol{N}_{m}, \boldsymbol{S}_{m}\right) ;
\end{array}
\end{aligned}
$$

end
Algorithm 1: Two-level Algorithm
Care must be taken in developing the smoother, as this is where most of the computational time is spent. The smoother used is a Red-Black Gauss-Seidel smoother, though we present one that is more Jacobi-like, as the implementation of the Gauss-Seidel method iterating over the black and red cells resembles the Jacobi method. We must solve for the $l+1$ iterate
in

$$
\begin{align*}
\phi_{i}^{l+1}(j, k) & +\frac{s}{h^{2}}\left(M_{i}\left(j+\frac{1}{2}, k\right)+M_{i}\left(j-\frac{1}{2}, k\right)+M_{i}\left(j, k+\frac{1}{2}\right)+M_{i}\left(j, k-\frac{1}{2}\right)\right) \mu_{i}^{l+1}(j, k) \\
& -\frac{s}{h^{2}}\left(M_{i}\left(j-\frac{1}{2}, k\right) \mu_{i}^{l}(j-1, k)+M_{i}\left(j+\frac{1}{2}, k\right) \mu_{i}^{l}(j+1, k)\right) \\
& -\frac{s}{h^{2}}\left(M_{i}\left(j, k-\frac{1}{2}\right) \mu_{i}^{l}(j, k-1)+M_{i}\left(j, k+\frac{1}{2}\right) \mu_{i}^{l}(j, k+1)\right) \\
& +\frac{s}{h^{2}}\left(M_{i}\left(j+\frac{1}{2}, k\right)+M_{i}\left(j-\frac{1}{2}, k\right)+M_{i}\left(j, k+\frac{1}{2}\right)+M_{i}\left(j, k-\frac{1}{2}\right)\right) p_{i}^{l+1}(j, k) \\
& -\frac{s}{h^{2}}\left(M_{i}\left(j-\frac{1}{2}, k\right) p_{i}^{l}(j-1, k)+M_{i}\left(j+\frac{1}{2}, k\right) p_{i}^{l}(j+1, k)\right) \\
& -\frac{s}{h^{2}}\left(M_{i}\left(j, k-\frac{1}{2}\right) p_{i}^{l}(j, k-1)+M_{i}\left(j, k+\frac{1}{2}\right) p_{i}^{l}(j, k+1)\right) \\
& -\stackrel{\circ}{\rho}_{i}^{-1} S_{i}^{l+1}(j, k) \\
& =F_{\phi_{i}} \tag{S-15}
\end{align*}
$$

$$
\begin{align*}
\mu_{i}^{l+1}(j, k) & -\frac{4\left(\epsilon_{i}^{2}+\epsilon_{\mathrm{sv}}^{2}\right)}{h^{2}} \phi_{i}^{l+1}(j, k) \\
& +\frac{\left(\epsilon_{i}^{2}+\epsilon_{\mathrm{sv}}^{2}\right)}{h^{2}}\left(\phi_{i}^{l}(j+1, k)+\phi_{i}^{l}(j-1, k)+\phi_{i}^{l}(j, k+1)+\phi_{i}^{l}(j, k-1)\right) \\
& -\sum_{\alpha \neq i, \alpha \neq \mathrm{sv}} \frac{4\left(\epsilon_{\mathrm{sv}}^{2}\right)}{h^{2}} \phi_{\alpha}^{l+1}(j, k)  \tag{S-16}\\
& +\sum_{\alpha \neq i, \alpha \neq \mathrm{sv}} \frac{\epsilon_{\mathrm{sv}}^{2}}{h^{2}}\left(\phi_{\alpha}^{l}(j+1, k)+\phi_{\alpha}^{l}(j-1, k)+\phi_{\alpha}^{l}(j, k+1)+\phi_{\alpha}^{l}(j, k-1)\right) \\
& =F_{\mu_{i}}
\end{align*}
$$

$$
\begin{align*}
& \frac{1}{h^{2}}\left(M_{p}\left(j+\frac{1}{2}, k\right)+M_{p}\left(j-\frac{1}{2}, k\right)+M_{p}\left(j, k+\frac{1}{2}\right)+M_{p}\left(j, k-\frac{1}{2}\right)\right) p^{l+1}(j, k) \\
& -\frac{1}{h^{2}}\left(M_{p}\left(j+\frac{1}{2}, k\right) p^{l}(j+1, k)+M_{p}\left(j, k+\frac{1}{2}\right) p^{l}(j, k+1)\right) \\
& -\frac{1}{h^{2}}\left(M_{p}\left(j-\frac{1}{2}, k\right) p^{l}(j-1, k)+M^{p}\left(j, k-\frac{1}{2}\right) p^{l}(j, k-1)\right) \\
& +\sum_{\alpha \neq \mathrm{sv}}\left(\frac{1}{h^{2}}\left(M_{\alpha}\left(j+\frac{1}{2}, k\right)+M_{\alpha}\left(j-\frac{1}{2}, k\right)+M_{\alpha}\left(j, k+\frac{1}{2}\right)+M_{\alpha}\left(j, k-\frac{1}{2}\right)\right) \mu_{\alpha}^{l+1}(j, k)\right. \\
& -\frac{1}{h^{2}}\left(M_{\alpha}\left(j+\frac{1}{2}, k\right) \mu_{\alpha}^{l}(j+1, k)+M_{\alpha}\left(j, k+\frac{1}{2}\right) \mu_{\alpha}^{l}(j, k+1)\right) \\
& \left.-\frac{1}{h^{2}}\left(M_{\alpha}\left(j-\frac{1}{2}, k\right) \mu_{\alpha}^{l}(j-1, k)+M_{\alpha}\left(j, k-\frac{1}{2}\right) \mu_{\alpha}^{l}(j, k-1)\right)\right) \\
& \left.+\left(-\stackrel{\circ}{\rho}_{\mathrm{sl}}^{-1}+\stackrel{\circ}{\rho}_{\mathrm{sv}}^{-1}\right) S_{i}^{l+1}(j, k)=0 . \quad \text { (here } M_{p}=\sum_{k} M_{i}\right) . \tag{S-17}
\end{align*}
$$

For this system, at every grid point we have to solve the system of equations of the form

$$
\left[\begin{array}{ccccccc}
a_{11} & a_{12} & 0 & 0 & 0 & 0 & a_{17}  \tag{S-18}\\
a_{21} & a_{22} & a_{23} & 0 & a_{25} & 0 & 0 \\
0 & 0 & a_{33} & a_{34} & 0 & 0 & a_{37} \\
a_{41} & 0 & a_{43} & a_{44} & a_{45} & 0 & 0 \\
0 & 0 & 0 & 0 & a_{55} & a_{56} & a_{57} \\
a_{61} & 0 & a_{63} & 0 & a_{65} & a_{66} & 0 \\
0 & a_{72} & 0 & a_{74} & 0 & a_{76} & a_{77}
\end{array}\right]\left[\begin{array}{c}
\phi_{s l}^{l+1}(j, k) \\
\mu_{s l}^{l+1}(j, k) \\
\phi_{p}^{l+1}(j, k) \\
\mu_{p}^{l+1}(j, k) \\
\phi_{q}^{l+1}(j, k) \\
\mu_{q}^{l+1}(j, k) \\
p^{l+1}(j, k)
\end{array}\right]=R H S
$$

on every cell $(j, k)$.
Typically some decoupling strategy takes place in the smoother so as to reduce computation time, since solving this 7 x 7 system of equations on every cell for a fully coupled system is computationally expensive. One effective strategy to decouple the system is to move the pressure coupling terms $a_{17}, a_{37}$, and $a_{67}$ in the $\phi_{i}$ equations and the all of the coupling terms
in the $\mu_{i}$ equations, except the corresponding $\phi_{i}$ term, to the right hand side to get the system

$$
\begin{align*}
& {\left[\begin{array}{ccccccc}
a_{11} & a_{12} & 0 & 0 & 0 & 0 & 0 \\
a_{21} & a_{22} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & a_{33} & a_{34} & 0 & 0 & 0 \\
0 & 0 & a_{43} & a_{44} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & a_{55} & a_{56} & 0 \\
0 & 0 & 0 & 0 & a_{65} & a_{66} & 0 \\
0 & a_{72} & 0 & a_{74} & 0 & a_{76} & a_{77}
\end{array}\right]\left[\begin{array}{l}
\phi_{s l}^{l+1}(j, k) \\
\mu_{s l}^{l+1}(j, k) \\
\phi_{p}^{l+1}(j, k) \\
\mu_{p}^{l+1}(j, k) \\
\phi_{q}^{l+1}(j, k) \\
\mu_{q}^{l+1}(j, k) \\
p^{l+1}(j, k)
\end{array}\right]=R H S} \\
& {\left[\begin{array}{c}
a_{17} p^{l}(j, k) \\
a_{23} \phi_{p}^{l}(j, k)+a_{25} \phi_{q}^{l}(j, k) \\
a_{37} p^{l}(j, k) \\
a_{41} \phi_{s l}^{l}(j, k)+a_{45} \phi_{q}^{l}(j, k) \\
a_{57} p^{l}(j, k) \\
a_{61} \phi_{s l}^{l}(j, k)+a_{63} \phi_{p}^{l}(j, k) \\
0
\end{array}\right] .} \tag{S-19}
\end{align*}
$$

This results in 3 block 2 by 2 matrix equations, which can be inverted readily. Then, once those chemical potentials have been updated, the pressure Poisson equation can be solved.

To improve stability and ensure logarithms are not evaluated for values less than or equal to zero, we regularize the logarithm ${ }^{3}$ by using the Taylor expansion of the logarithm function about $\delta$ for $x<\delta$ so that

$$
\ln _{\delta}(x)= \begin{cases}\ln (x) & x>\delta  \tag{S-20}\\ \ln (\delta)+2 \frac{x}{\delta}-\frac{x^{2}}{2 \delta^{2}}-1.5 & x \leq \delta\end{cases}
$$

for a small parameter $\delta$ which is taken to be $10^{-3}$ in simulations presented in this work. This
is an approximation to the logarithm function which is $C^{2}$ and which has the property that on $[\delta, \infty)$ its derivative and second derivative match that of the logarithm function, as

$$
\begin{equation*}
\left.\frac{d}{d x} \ln _{\delta}(x)\right|_{x=\delta}=\frac{2}{\delta}-\frac{1}{\delta}=\frac{1}{\delta} \tag{S-21}
\end{equation*}
$$

and

$$
\begin{equation*}
\left.\frac{d^{2}}{d x^{2}} \ln _{\delta}(x)\right|_{x=\delta}=-\frac{1}{\delta^{2}} \tag{S-22}
\end{equation*}
$$

## Rayleighian approach

Here, we show that the Rayleighian approach based on the Onsager's variational principle ${ }^{44 / 7}$ will lead to the same set of equations. As already mentioned in the main text, this approach involves a priori knowledge of the mechanism leading to dissipation of energy without any prescription of deriving a so-called dissipation function. In the following, we use the relation between the rate of the change of the free energy with the disspiation function as prescribed by the Onsager's variational principle. This allows us to identify the dissipation function and construct an appropriate Rayleighian, which when optimized with respect to the velocities and sources lead to an identical set of equations as presented in the main text.

The Rayleighian is a functional, which includes rate of change of the free energy $\left(\dot{F}_{u}\right)$, the dissipation function $(\Phi)$ and constraints included via the methods of the Lagrange's multipliers $(C)$. As the dissipation function is only related to the fluxes, in general, we can write

$$
\begin{align*}
R\left[\left\{\phi_{i}, \boldsymbol{u}_{i}, S_{i},\left.\boldsymbol{u}_{i} \cdot \boldsymbol{n}\right|_{\Gamma}\right\}\right] & =\dot{F}_{u}\left[\left\{\phi_{i}, \boldsymbol{u}_{i}, S_{i},\left.\boldsymbol{u}_{i} \cdot \boldsymbol{n}\right|_{\Gamma}\right\}\right]+\Phi\left[\left\{\boldsymbol{u}_{i}, S_{i},\left.\boldsymbol{u}_{i} \cdot \boldsymbol{n}\right|_{\Gamma}\right\}\right]  \tag{S-23}\\
& +C\left[\left\{\phi_{i}, \boldsymbol{u}_{i}, S_{i},\left.\boldsymbol{u}_{i} \cdot \boldsymbol{n}\right|_{\Gamma}\right\}\right]
\end{align*}
$$

where $\phi_{i}$ is the volume fraction of $i$ th component, $\boldsymbol{u}_{i}$ and $S_{i}$ are the velocities and sources/sinks, respectively, in the interior of volume $(\Omega)$ with boundaries $\Gamma$ (see Fig. 1 in the main text).
$\boldsymbol{u}_{i} \cdot \boldsymbol{n}$ is the normal component of the velocities at the boundaries. It is to be noted that the dissipation function only depends on $\boldsymbol{u}_{i}$ and $S_{i}$ without any explicit dependence on the volume fractions, $\phi_{i}$.

As per the variational principle leading to maximal rate of entropy generation requires (e.g., see Eq. 5.10 in Ref. ${ }^{[4}$ and SI in Ref. ${ }^{[7]}$

$$
\begin{equation*}
\dot{F}_{u}\left[\left\{\phi_{i}, \boldsymbol{u}_{i}, S_{i},\left.\boldsymbol{u}_{i} \cdot \boldsymbol{n}\right|_{\Gamma}\right\}\right]+C\left[\left\{\phi_{i}, \boldsymbol{u}_{i}, S_{i},\left.\boldsymbol{u}_{i} \cdot \boldsymbol{n}\right|_{\Gamma}\right\}\right]=-2 \Phi\left[\left\{\boldsymbol{u}_{i}, S_{i},\left.\boldsymbol{u}_{i} \cdot \boldsymbol{n}\right|_{\Gamma}\right\}\right] \tag{S-24}
\end{equation*}
$$

Now, $\dot{F}_{u}+C=\dot{F}$, which is given by Eq. 19 in the main text. This, in turn, means that the right hand side of Eq. 19 allows us to identify the dissipation function readily. Eliminating $\phi_{i}, \mu_{i}$ and $p$ to rewrite the right hand side solely in terms of $\boldsymbol{u}_{i}, S_{i}$ and $\boldsymbol{u}_{i} \cdot \boldsymbol{n}$ using the constitutive equations (Eqs. 16-18 in the main text) along with the local equilibrium boundary conditions, leads to the realization that

$$
\begin{align*}
\Phi\left[\left\{\boldsymbol{u}_{i}, S_{i},\left.\boldsymbol{u}_{i} \cdot \boldsymbol{n}\right|_{\Gamma}\right\}\right]= & \sum_{i}\left[\frac{1}{2 \gamma_{i}} \int_{\Omega}\left|\boldsymbol{u}_{i}(\boldsymbol{x}, t)\right|^{2} d \boldsymbol{x}+\frac{1}{2 \omega_{i}} \int_{\Gamma_{\text {top }}}\left|\boldsymbol{u}_{i}(\boldsymbol{x}, t) \cdot \boldsymbol{n}\right|^{2} d \boldsymbol{\sigma}\right] \\
& +\frac{1}{2 \lambda} \int_{\Omega} S_{\mathrm{sl}}^{2}(\boldsymbol{x}, t) d \boldsymbol{x} \tag{S-25}
\end{align*}
$$

Here, similar to the main text, we have suppressed the functional dependencies of the coefficients $\gamma_{i}, \omega_{i}$ and $\lambda$ on the volume fractions, which need to be determined from a microscopic approach. This leads to the Rayleighian, written as

$$
\begin{align*}
R= & \sum_{i}\left[\int_{\Omega} \phi_{i}(\boldsymbol{x}, t) \nabla\left(\mu_{i}(\boldsymbol{x}, t)+p(\boldsymbol{x}, t)\right) \cdot \boldsymbol{u}_{i}(\boldsymbol{x}, t) d \boldsymbol{x}\right. \\
& -\int_{\Gamma_{\text {top }}} \phi_{i}(\boldsymbol{x}, t)\left(\mu_{i}(\boldsymbol{x}, t)+p(\boldsymbol{x}, t)\right) \boldsymbol{u}_{i}(\boldsymbol{x}, t) \cdot \boldsymbol{n} d \boldsymbol{\sigma} \\
& \left.+\frac{1}{2 \gamma_{i}} \int_{\Omega}\left|\boldsymbol{u}_{i}(\boldsymbol{x}, t)\right|^{2} d \boldsymbol{x}+\frac{1}{2 \omega_{i}} \int_{\Gamma_{\text {top }}}\left|\boldsymbol{u}_{i}(\boldsymbol{x}, t) \cdot \boldsymbol{n}\right|^{2} d \boldsymbol{\sigma}\right]+\frac{1}{2 \lambda} \int_{\Omega} S_{\mathrm{sl}}^{2}(\boldsymbol{x}, t) d \boldsymbol{x} \\
& +\int_{\Omega}\left[\stackrel{\circ}{\mathrm{sl}}_{-1} \mu_{\mathrm{sl}}(\boldsymbol{x}, t)-\stackrel{\circ}{\mathrm{sv}}_{-1} \mu_{\mathrm{sv}}(\boldsymbol{x}, t)+\left(\stackrel{\circ}{\mathrm{sl}}_{-1}^{-1}-\stackrel{\circ}{\mathrm{sv}}_{-1}^{\text {an }}\right) p(\boldsymbol{x}, t)\right] S_{\mathrm{sl}}(\boldsymbol{x}, t) d \boldsymbol{x} \tag{S-26}
\end{align*}
$$

Optimizing the Rayleighian with respect to $\boldsymbol{u}_{i}, S_{i}$ and $\boldsymbol{u}_{i}(\boldsymbol{x}, t) \cdot \boldsymbol{n}$ leads to the same sets of equations as the Eqs. 16-18 in the main text. In particular,

$$
\begin{gather*}
\frac{\delta R}{\delta \boldsymbol{u}_{i}}=\phi_{i}(\boldsymbol{x}, t) \nabla\left(\mu_{i}(\boldsymbol{x}, t)+p(\boldsymbol{x}, t)\right)+\gamma_{i}^{-1} \boldsymbol{u}_{i}(\boldsymbol{x}, t)=0  \tag{S-27}\\
\frac{\delta R}{\delta S_{\mathrm{sl}}}=\lambda^{-1} S_{\mathrm{sl}}(\boldsymbol{x}, t)+\stackrel{\circ}{\mathrm{sl}}_{-1}^{{ }_{\mathrm{sl}}} \mu_{\mathrm{sl}}(\boldsymbol{x}, t)-\stackrel{\circ}{\rho}_{\mathrm{sv}}^{-1} \mu_{\mathrm{sv}}(\boldsymbol{x}, t)+\left(\stackrel{\circ}{\mathrm{sv}}_{-1}^{-1} \stackrel{\circ}{\mathrm{sl}}_{-1}\right) p(\boldsymbol{x}, t)=0 \tag{S-28}
\end{gather*}
$$

and

$$
\begin{equation*}
\frac{\delta R}{\delta\left(\boldsymbol{u}_{i} \cdot \boldsymbol{n}\right)}=\omega_{i}^{-1} \boldsymbol{u}_{i}(\boldsymbol{x}, t) \cdot \boldsymbol{n}-\phi_{i}(\boldsymbol{x}, t)\left(\mu_{i}(\boldsymbol{x}, t)+p(\boldsymbol{x}, t)\right)=0 \tag{S-29}
\end{equation*}
$$

at the top boundary.

## Additional simulation results

We have executed simulations with the identical parameter set as those used in generating Fig. 7 in the main text. However, instead of using a concentration dependent $\gamma_{i}$, which leads to kinetic freezing, we have taken $\gamma_{i}$ to be independent of the volume fractions. For this case, results are shown in Fig. S3. In contrast to the Fig. 7 in the main text, pillars are formed instead of a much rougher film seen in there.

## References

(1) Trottenberg, U.; Oosterlee, C.; Schüller, A. Multigrid; Academic Press, 2001.
(2) Wise, S.; Kim, J.; Lowengrub, J. Solving the regularized, strongly anisotropic CahnHilliard equation by an adaptive nonlinear multigrid method. Journal of Computational Physics 2007, 226, 414 - 446.
(3) Jeong, D.; Kim, J. A practical numerical scheme for the ternary Cahn-Hilliard system with a logarithmic free energy. Physica A: Statistical Mechanics and its Applications 2016, 442, 510-522.


Fig. S1: Flory-Huggins free energy surface $\left(f_{h} / k_{B} T\right.$, given by Eq. 40 in the main text, with vapor being the zeroth component) for a ternary mixture with parameters, $N_{0}=N_{1}=N_{2}=$ $1, \stackrel{\circ}{\rho}_{0}=0.001, c=0, \stackrel{\circ}{\rho}_{1}=\stackrel{\circ}{\rho}_{2}=1.0, \chi_{01}=\chi_{02}=1.2, \chi_{12}=0.9$.


Fig. S2: Flory-Huggins free energy surface $\left(f_{h} / k_{B} T\right.$, given by Eq. 40 in the main text, with vapor being the zeroth component) for a ternary mixture with parameters, $N_{0}=N_{1}=N_{2}=$ $1, \stackrel{\circ}{\rho}_{0}=0.001, c=0.2, \stackrel{\circ}{\rho}_{1}=\stackrel{\circ}{\rho}_{2}=1.0, \chi_{01}=\chi_{02}=1.2, \chi_{12}=0.9$. It is shown that minimum in the free energy surface is near $\phi_{0} \approx 1$ so that the phase with high volume fraction of the component 0 is energetically favorable.


Fig. S3: (a) Plot of $\phi_{q}$ is shown here exhibiting enhanced phase separation near the vaporpolymer blend interface. (b)-(c) More regular pillar-like structures start to emerge in contrast to the volume fraction dependent $\gamma_{i}$. (d) The pillar like structures stay stabilized.
(4) Onsager, L. Reciprocal Relations in Irreversible Processes. I. Physical Review 1931, 37, 405.
(5) Doi, M.; Onuki, A. Dynamic coupling between stress and composition in polymer solutions and blends. Journal de Physique II 1992, 2, 1631-1656.
(6) Doi, M. Onsager's variational principle in soft matter. Journal of Physics: Condensed Matter 2011, 23, 284118.
(7) Kumar, R.; Mahalik, J. P.; Bocharova, V.; Stacy, E. W.; Gainaru, C.; Saito, T.; Gobet, M. P.; Greenbaum, S.; Sumpter, B. G.; Sokolov, A. P. A Rayleighian approach for modeling kinetics of ionic transport in polymeric media. The Journal of Chemical Physics 2017, 146, 064902.

