

Supplementary material for “Diffusive dynamics and electrochemical regulation of weak polyelectrolytes across liquid interfaces”

Giulia L Celora*

*University College London, Department of Mathematics,
25 Gordon Street, London, WC1H 0AY, UK and*

Mathematical Institute, University of Oxford, Andrew Wiles Building, Woodstock Road, Oxford OX2 6GG, UK

Ralf Blossey†

University of Lille, Unité de Glycobiologie Structurale et Fonctionnelle (UGSF), CNRS UMR8576, F-59000 Lille, France

Andreas Münch‡

Mathematical Institute, University of Oxford, Andrew Wiles Building, Woodstock Road, Oxford OX2 6GG, UK

Barbara Wagner§

Weierstrass Institute, Mohrenstr. 39, 10117 Berlin, Germany

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SMI. NON-DIMENSIONAL FORM OF THE MODELLING EQUATIONS

We here present the procedure used to non-dimensionalise the model presented in Section II specialised to a 1D geometry, $\Omega = [0, L]$. To do so, we introduce the following dimensionless variables

$$\begin{aligned}
 \phi_m = \nu_m c_m, \quad \hat{j}_m = j_m \frac{L_\psi \nu_m}{D}, \quad \tau = \frac{D}{L_\psi^2} t, \quad \hat{x} = \frac{x}{L_\psi}, \quad \hat{f}_{\text{eff}} = \frac{\bar{f}_{\text{eff}} \nu}{k_B T}, \quad \hat{\mu}_\beta^{\text{el}} = \frac{\mu_\beta^{\text{el}} \nu}{k_B T \nu_\beta}, \quad \hat{P} = \frac{(P - \bar{P}) \nu}{k_B T}, \\
 \hat{u}_{\text{CR},s}^1 = \frac{u_{\text{CR},s}^1 - u_{\text{CR},s}^0}{k_B T}, \quad \hat{u}_{\text{CR},p}^q = \frac{u_{\text{CR},p}^q}{k_B T} - \hat{u}_{\text{CR},s}^1, \quad \hat{\mu}_H^{\text{el}} = \frac{\mu_H}{k_B T} - \hat{u}_{\text{CR},s}^1, \quad \hat{\lambda}_{\text{CR}} = \lambda_{\text{CR}} + \frac{e\psi}{k_B T} + \hat{u}_{\text{CR},s}^1, \\
 \hat{\psi} = \frac{\psi e}{k_B T}, \quad \hat{\rho} = \rho \nu, \quad \hat{q}_p = \frac{q_p}{N}, \quad L_\psi = \sqrt{\frac{\epsilon \nu k_B T}{e^2}},
 \end{aligned} \tag{S-1}$$

* giulia.celora@maths.ox.ac.uk

† ralf.blossey@univ-lille.fr

‡ muench@maths.ox.ac.uk

§ barbara.wagner@wias-berlin.de

and reformulate the modelling equations on the interval $\hat{x} \in (0, \ell_\Omega)$

$$\partial_\tau \phi_m - \partial_{\hat{x}} \cdot \left(\sum_K \hat{\mathcal{M}}_{mK} \partial_{\hat{x}} \hat{\mu}_K^{\text{el}} \right) = 0, \quad m \in \mathcal{I}_H \quad (\text{S-2a})$$

$$-\partial_{\hat{x}}^2 \hat{\psi} = \phi_H + \phi_+ - \phi_-, \quad (\text{S-2b})$$

with the rescaled mobility matrix

$$\mathcal{M} = \begin{bmatrix} \phi_p & 0 & \hat{q}_p \phi_p & 0 & 0 \\ 0 & \phi_s & q_s \phi_s & 0 & 0 \\ \hat{q}_p \phi_p & q_s \phi_s & \langle q^2 \rangle_s \phi_s + \frac{\langle q^2 \rangle_p}{N^2} \phi_p & 0 & 0 \\ 0 & 0 & 0 & \phi_+ & 0 \\ 0 & 0 & 0 & 0 & \phi_- \end{bmatrix} \quad (\text{S-3a})$$

and the rescaled electrochemical potentials

$$\hat{\mu}_\pm^{\text{el}} = \hat{P} \pm \hat{\psi} + \frac{\partial \hat{f}_{\text{eff}}}{\partial \phi_\pm}, \quad (\text{S-3b})$$

$$\hat{\mu}_s^{\text{el}} = \hat{P} + q_s \hat{\psi} + \frac{\partial \hat{f}_{\text{eff}}}{\partial \phi_s}, \quad (\text{S-3c})$$

$$\hat{\mu}_p^{\text{el}} = \hat{P} + \hat{q}_p \hat{\psi} + \frac{\partial \hat{f}_{\text{eff}}}{\partial \phi_p} - \ell_\kappa^2 \partial_{\hat{x}}^2 \phi_p, \quad (\text{S-3d})$$

$$\hat{\mu}_H^{\text{el}} = -\hat{\lambda}_{\text{CR}} + \hat{\psi}, \quad (\text{S-3e})$$

where the rescaled thermodynamic pressure and free energy are respectively

$$\hat{P} = \hat{f}_{\text{eff}} - \sum_{i \in \mathcal{I}} \phi_i \frac{\partial \hat{f}_{\text{eff}}}{\partial \phi_i} + \frac{1}{2} \left(\partial_{\hat{x}} \hat{\psi} \right)^2 + \ell_\kappa^2 \left(\phi_p \partial_{\hat{x}}^2 \phi_p - \frac{(\partial_{\hat{x}} \phi_p)^2}{2} \right), \quad (\text{S-3f})$$

$$\hat{f}_{\text{eff}} = \phi_+ \ln \phi_+ + \phi_- \ln \phi_- + \frac{\phi_p}{N} \left(\ln \left(\frac{\phi_p}{\mathcal{Z}_p(\hat{\lambda}_H)} \right) + \hat{q}_p \hat{\psi} \right) - \phi_s \left(\ln \left(\frac{\phi_s}{\mathcal{Z}_s(\hat{\lambda}_H)} \right) + q_s \hat{\psi} \right) - \phi_H \hat{\lambda}_H. \quad (\text{S-3g})$$

The local mean charges on the polymer and solvent phases are

$$\hat{q}_p = -\frac{1}{N} \frac{d}{d\hat{\lambda}_H} \ln \mathcal{Z}_p(\hat{\lambda}_H), \quad q_s = -\frac{d}{d\hat{\lambda}_H} \ln \mathcal{Z}_s(\hat{\lambda}_H) \quad (\text{S-4a})$$

$$\mathcal{Z}_s = \sum_{\zeta=0}^1 \exp \left(-\hat{\lambda}_{\text{CR}} \zeta \right), \quad \mathcal{Z}_p = \sum_{\zeta=0}^{Q_p} \exp \left(-(\hat{u}_{\text{CR},p}^\zeta + \hat{\lambda}_{\text{CR}} \zeta) \right), \quad (\text{S-4b})$$

with the Lagrange multiplier $\hat{\lambda}_{\text{CR}}$ being defined by the constraint

$$\phi_H - \hat{q}_p \phi_p - q_s \phi_s = 0. \quad (\text{S-4c})$$

The problem is then closed by imposing boundary conditions

$$\partial_{\hat{x}} \hat{\psi}(0, t) = \partial_{\hat{x}} \hat{\psi}(\ell_\Omega, t) = 0, \quad (\text{S-5a})$$

$$\hat{j}_m(0, t) = \hat{j}_m(\ell_\Omega, t) = 0, \quad m \in \mathcal{I}_H, \quad (\text{S-5b})$$

$$\int_0^{\ell_\Omega} \hat{\psi}(x, t) dx = 0, \quad (\text{S-5c})$$

and appropriate initial conditions

$$\phi_m(x, 0) = \phi_m^0(x), \quad x \in [0, \ell_\Omega], \quad m \in \mathcal{I}_H, \quad (\text{S-5d})$$

where the initial data must be $\phi_i^0(x) \in (0, 1)$ and satisfy global electroneutrality,

$$\int_0^{\ell_\Omega} (\phi_H^0 + \phi_+^0 - \phi_-^0) dx = 0,$$

and the local no-void conditions

$$\phi_s^0(x) = 1 - \phi_p^0(x) - \phi_+^0(x) - \phi_-^0(x).$$

The rescaled version of the model highlights the presence of a key non-dimensional parameter

$$\ell_\kappa = \frac{1}{L_\psi} \sqrt{\frac{\kappa}{k_B T \nu N^2}}.$$

which is a measure of the competition between the short- (*i.e.*, interfacial) and long-range (*i.e.*, Coulombic) interactions. Note that the choice of scaling the spatial dimension by the Debye-length L_ψ follows the literature on dilute electrolytes [1]. However, the screening length for weak polyelectrolytes differs as investigated in Section SMIII.

SMII. DYNAMICAL SIMULATIONS

We solve the non-dimensional form of the modelling equations, Eqs. (S-2)-(S-5) using the method of lines. We first discretise Eqs. (S-2) in space using a finite volume scheme over a stencil of $N_x = 500$ points to obtain a system of $4N_x$ ODEs, which are coupled to a system of N_x algebraic equations for λ_{CR} . The differential-algebraic system of equations is solved over time using `DifferentialEquations.jl` package [2] in `Julia`. The values of the model parameters used to generate the Figures are listed in Table SM1.

For the charge-regulation dynamics, we use the standard linear-quadratic form for the charge regulation energy as in [3, 4],

$$\hat{u}_{\text{CR},p}^q = \alpha q + \frac{\eta}{2Q_p} q^2 - \ln \left[\binom{Q_p}{q} \right], \quad (\text{S-6})$$

where we take $\alpha < 0$ and large ($|\alpha| \gg 1$), so that it is energetically favourable for a proton to bind to the polymer, and set $\eta \geq 0$ to capture the repulsive short-range attraction between charges bounded to the polymer. As shown in [3], the equilibrium behaviour of the system is qualitatively independent of the precise value of η as long as $\eta \geq 0$.

TABLE SM1: Default value(s) of the non-dimensional model parameters used in the dynamical simulations of Eqs. (S-2)-(S-5) and scaling factors to convert variables to dimensional units.

Parameter	Description	Value
ℓ_κ	ratio of the interfacial and Debye length L_ψ	10
ℓ_Ω	Domain size relative to the Debye length L_ψ	500
α	binding energy of protons to ionizable residues relative to thermal energy	-7.0
η	interaction energy of protons bound to the same polymer chain relative to thermal energy	3.
χ	Flory-Huggins constant	1.5
Z	number of ionizable monomers for polymer chain	4
N	number of monomers for polymer [5]	10
ϕ_P^0	spatially averaged polymer volume fraction [5]	0.1
ϕ_+^0	spatially averaged salt volume fraction	0.001
ϕ_H^0	spatially averaged protonised molecules volume fraction	0.0001-0.4
L_ψ	Debye length scale of water at room temperature	$\approx 0.1 - 10$ nm
$T = L_\psi^2 \ell_\Omega^2 D^{-1}$	Characteristic temporal scale, taken to be the timescale associated with diffusion	$\approx 10^{-4} - 10^{-2}$ [s]
D	Diffusion coefficient of ions and solvent	10^{-9} [m ² /s]
$(\nu N_A)^{-1}$	conversion from volume fraction to moles	55.35 [M]
ν	molecular volume of water	0.03 nm ³
N_A	Avogadro Number	6.022×10^{23} [mol ⁻¹]

SMIII. STABILITY ANALYSIS

We here present the derivation of the dispersion relation for the model presented in Section II used in generating Figure 4 and the corresponding spinodal curves illustrated in Figure 5.

A. Dispersion relation

While the conservative formulation of the model in Section SMI is the most appropriate for dynamical simulations, it leads to unnecessary complications in the derivation of the dispersion relation. To simplify this analysis, we rewrite the model by replacing the mass conservation equation for ϕ_H with a dynamic equation for q_s . In other words, we now consider the fraction of charges on the solvent molecules as an unknown variable, while ϕ_H is computed a posteriori. Note that this transformation is possible despite q_s being a non-linear function of ϕ_H . As mentioned in the main text, the mapping between the two variables is implicitly defined by

$$\mathcal{C}(q_s) = q_s \phi_s - \phi_H + \hat{q}_p(q_s) \phi_p = 0, \quad q_s, \phi_s, \phi_H, \phi_p \in (0, 1)^4. \quad (\text{S-7})$$

When taking the derivative of the function $\mathcal{C}(q_s)$ with respect to its argument q_s , the latter is positive for any value of $q_s \in (0, 1)$. Invoking the Implicit Function Theorem, we therefore have that $q_s(\phi_H) : (0, 1) \rightarrow (0, 1)$ is invertible. Therefore, we can equivalently define our system in terms of the conserved variables $(\phi_p, \phi_+, \phi_-, \phi_s, \phi_H)$ or the transformed set of variables $(\phi_p, \phi_+, \phi_-, \phi_s, q_s)$. This choice of variables helps with the algebraic derivation of the dispersion relation because \hat{q}_p can be expressed directly as a function of q_s alone. By applying this change of variables, the problem can be rewritten in terms of the pseudo-free energy of the system, which then reads:

$$\bar{g}(\phi_p, \phi_+, \phi_-, \phi_s) = \phi_+ \ln \phi_+ + \phi_- \ln \phi_- + \phi_s \ln \phi_s + \frac{\phi_p}{N} \ln \phi_p + \chi \phi_s \phi_p, \quad (\text{S-8})$$

which is equivalent to the mixing free energy of a 4-component mixture. We note that here the introduction of the function \bar{g} is purely for the purpose of easing the analysis. The transport equations for the different components then take the standard form:

$$\partial_t \phi_m = \nabla \cdot \left(\phi_m \left(\nabla \left(\frac{\partial \bar{g}}{\partial \phi_m} \right) + \ell_\kappa^2 (\phi_p - \delta_{mp}) \nabla^3 \phi_p + (q_m - \varrho) \nabla \psi \right) \right), \quad (\text{S-9a})$$

and the electric field ψ satisfies

$$-\nabla^2 \psi = q_s \phi_s + q_p(q_s) \phi_p + \phi_+ - \phi_-. \quad (\text{S-9b})$$

Note that for simplicity, we have dropped the hat notation from q_p to indicate the rescaled polymer charge \hat{q}_p (see Eq. (S-1)). When compared to the previous formulation, here the cross-diffusion term with ϕ_H in the equations for ϕ_p and ϕ_s vanishes, being substituted by an electric current due to the average charge on each of the two charged species ($q_{p,s}$). Importantly, we now require an explicit equation for the evolution of q_s , which can be derived using Eq. (S-7)

$$\begin{aligned} \partial_t q_s &= \frac{\partial_t \phi_H - q_p(q_s) \partial_t \phi_p - q_s \partial_t \phi_s}{\phi_s + \phi_p q'_p(q_s)} \\ &= \frac{\sigma_s}{\phi_s \sigma_s + \phi_p \sigma_p N} \nabla \cdot \left((\phi_s \sigma_s + \phi_p \sigma_p) \nabla \left(\ln \frac{q_s}{1 - q_s} + \psi \right) \right) - \frac{\sigma_s \mathbf{j}_s + \sigma_p N \mathbf{j}_p}{\phi_s \sigma_s + \phi_p \sigma_p N} \cdot \nabla q_s. \end{aligned} \quad (\text{S-9c})$$

where $\sigma_s = q_s(1 - q_s) \in (0, 1)$ and $\sigma_p = \langle q^2 \rangle_p / N^2 - q_p^2$ can be interpreted as the variance of the charge distribution on the solvent and polymer molecules, respectively. Note again that here σ_p is normalised by the total number of monomers on a polymer chain N . When considering the linear stability analysis, the function q_s can be expressed as

$$q_s = q_s^0 + \delta \sum_{r \in \mathbb{N}} U_\varrho^r \cos(r\pi x) e^{\omega t}, \quad (\text{S-10})$$

where U_ϱ^r is connected to the amplitude of the perturbations in the original variables by

$$U_\varrho^r = \sigma_s^0 \frac{U_H^r - q_p^0 U_p^r - q_s^0 U_s^r}{\sigma_s^0 \phi_s^0 + \phi_p^0 \sigma_p^0 N}.$$

Using the above ansatz yields a linear 6-dimensional algebraic system for $\mathbf{U}^r = (U_p^r, U_+^r, U_-^r, U_s^r, U_\varrho^r, U_\psi^r)$, dependent on the wavenumber r and the corresponding growth rate ω . We can use the no-void condition and the Poisson equation to explicitly solve for U_s^r and U_ψ^r

$$U_s^r = -U_p^r - U_+^r - U_-^r, \quad (\text{S-11})$$

$$(r\pi)^2 U_\psi^r = (q_p^0 - q_s^0) U_p^r + (1 - q_s^0) U_+^r - (1 + q_s^0) U_-^r + \frac{\phi_p^0 \sigma_p^0 N + \sigma_s^0 \phi_s^0}{\sigma_s^0} U_\varrho^r = \sum_j q_j^* U_j^r, \quad (\text{S-12})$$

and reduce the problem to a linear 4-dimensional algebraic system that can be written as

$$\omega \left[\left(\frac{1}{\phi_p^0} + \frac{1}{\phi_s^0} \right) U_p^r + \frac{U_+^r}{\phi_s^0} + \frac{U_-^r}{\phi_s^0} \right] = -(r\pi)^2 \sum_i G_{pi}^0 U_i^r - q_p^* \sum_j q_j^* U_j^r - \ell_\kappa^2 (r\pi)^4 U_p^r, \quad (\text{S-13a})$$

$$\omega \left[\frac{1}{\phi_s^0} U_p^r + \left(\frac{1}{\phi_+^0} + \frac{1}{\phi_s^0} \right) U_+^r + \frac{U_-^r}{\phi_s^0} \right] = -(r\pi)^2 \sum_i G_{+i}^0 U_i^r - q_+^* \sum_j q_j^* U_j^r, \quad (\text{S-13b})$$

$$\omega \left[\frac{1}{\phi_s^0} U_p^r + \frac{U_+^r}{\phi_s^0} + \left(\frac{1}{\phi_-^0} + \frac{1}{\phi_s^0} \right) U_-^r \right] = -(r\pi)^2 \sum_i G_{-i}^0 U_i^r - q_-^* \sum_j q_j^* U_j^r, \quad (\text{S-13c})$$

$$\omega \frac{(q_\varrho^*)^2}{\phi_p^0 \sigma_p^0 + \sigma_s^0 \phi_s^0} U_\varrho^r = -(r\pi)^2 \frac{q_\varrho^*}{\sigma_s^0} U_\varrho^r - q_\varrho^* \sum_j q_j^* U_j^r. \quad (\text{S-13d})$$

where the index i only sums over $+, -, p$, while j over $+, -, p, \varrho$, and G_{ki} indicate the second order partial derivatives of the function G

$$G(\phi_p, \phi_+, \phi_-) = \bar{g}(\phi_p, \phi_+, \phi_-, 1 - \phi_p - \phi_+ - \phi_-),$$

with respect to its arguments ϕ_k and ϕ_i . The system (S-13) can be written in matrix form as a generalised eigenvalue problem

$$\mathbf{A}_r \mathbf{U}^r = \omega \mathbf{B} \mathbf{U}^r,$$

where the mass matrix

$$\mathbf{B} = \frac{1}{\phi_s^0} \begin{bmatrix} \frac{\phi_p^0 + \phi_s^0}{\phi_p^0} & 1 & 1 & 0 \\ 1 & \frac{\phi_+^0 + \phi_s^0}{\phi_+^0} & 1 & 0 \\ 1 & 1 & \frac{\phi_-^0 + \phi_s^0}{\phi_-^0} & 0 \\ 0 & 0 & 0 & \frac{(q_\varrho^*)^2 \phi_s^0}{\phi_p^0 \sigma_p^0 + \sigma_s^0 \phi_s^0} \end{bmatrix} \quad (\text{S-14})$$

is symmetric and positive definite for all physical steady states, and the symmetric matrix \mathbf{A}_r is given by

$$\mathbf{A}_r = - \begin{bmatrix} (r\pi)^2 G_{pp}^0 + \ell_\kappa^2 (r\pi)^4 + (q_p^*)^2 & (r\pi)^2 G_{p+}^0 + q_p^* q_+^* & (r\pi)^2 G_{p-}^0 + q_p^* q_-^* & q_p^* q_\varrho^* \\ \star & (r\pi)^2 G_{++}^0 + (q_+^*)^2 & (r\pi)^2 G_{+-}^0 + q_+^* q_-^* & q_+^* q_\varrho^* \\ \star & \star & (r\pi)^2 G_{--}^0 + (q_-^*)^2 & q_-^* q_\varrho^* \\ \star & \star & \star & (r\pi)^2 \frac{q_\varrho^*}{\sigma_s^0} + (q_\varrho^*)^2 \end{bmatrix} \quad (\text{S-15})$$

where the \star symbols are used to avoid rewriting the entries already defined by the symmetry of the matrix \mathbf{A}_r .

B. Computation of the spinodal

To compute the boundary of the stability region of homogeneous solutions, we compute the values of the wavenumber r for which $\det(\mathbf{A}_r) = 0$, which is equivalent to finding conditions for which it exists a non-trivial solution to the

following 4D homogeneous algebraic system

$$0 = -(r\pi)^2 \sum_i G_{pi}^0 U_i^r - q_p^* \sum_j q_j^* U_j^r - \ell_\kappa^2 (r\pi)^4 U_p^r, \quad (\text{S-16a})$$

$$0 = -(r\pi)^2 \sum_i G_{\pm i}^0 U_i^r - q_\pm^* \sum_j q_j^* U_j^r, \quad (\text{S-16b})$$

$$0 = -(r\pi)^2 \frac{q_\varrho^*}{\sigma_s^0} U_\varrho^r - q_\varrho^* \sum_j q_j^* U_j^r. \quad (\text{S-16c})$$

Using Eqs. (S-16c) and (S-12), we find that there is a simple proportional relationship between the solvent mean charge and the electric field fluctuations; namely, $U_\varrho^r = \sigma_s^0 U_\psi^r$. We can, therefore, rewrite the above system in the form

$$0 = -(r\pi)^2 \left[\sum_i G_{pi}^0 U_i^r + q_p^* U_\psi + (\ell_\kappa r\pi)^2 U_p^r \right], \quad (\text{S-17a})$$

$$0 = -(r\pi)^2 \left[\sum_i G_{\pm i}^0 U_i^r + q_\pm^* U_\psi^r \right], \quad (\text{S-17b})$$

$$0 = -(r\pi)^2 U_\psi^r + q_p^* U_p^r + q_+^* U_+^r + q_-^* U_-^r + q_\varrho^* \sigma_s^0 U_\psi. \quad (\text{S-17c})$$

Since the system is conservative, we only consider perturbations with positive wavenumbers $r > 0$. Therefore, Eq. (S-17b) can be used to directly express U_\pm^r in terms of U_ψ and U_p independently of the wavenumber r :

$$U_\pm = a_{\pm p} U_p + a_{\pm \psi} U_\psi,$$

where

$$a_{+p}^0 = \frac{-G_{-+}^0 G_{p+}^0 + G_{+-}^0 G_{p-}^0}{G_{++}^0 G_{--}^0 - (G_{+-}^0)^2}, \quad a_{+\psi}^0 = \frac{-G_{-+}^0 \hat{q}_+ + G_{+-}^0 \hat{q}_-}{G_{++}^0 G_{--}^0 - (G_{+-}^0)^2}, \quad (\text{S-18a})$$

$$a_{-p}^0 = \frac{-G_{++}^0 G_{p-}^0 + G_{+-}^0 G_{p+}^0}{G_{++}^0 G_{--}^0 - (G_{+-}^0)^2}, \quad a_{-\psi}^0 = \frac{-G_{++}^0 \hat{q}_- + G_{+-}^0 \hat{q}_+}{G_{++}^0 G_{--}^0 - (G_{+-}^0)^2}. \quad (\text{S-18b})$$

Substituting the expression of U_\pm into Eq. (S-17a) and Eq. (S-17c), we obtain the following 2D algebraic system

$$\begin{bmatrix} 0 \\ 0 \end{bmatrix} = \underbrace{\begin{bmatrix} G_{pp}^0 + a_{p+} G_{p+}^0 + a_{p-} G_{p-}^0 + (\ell_\kappa r\pi)^2 & \hat{q}_p + a_{+\psi}^0 G_{p+}^0 + a_{-\psi}^0 G_{p-}^0 \\ \hat{q}_p + a_{p+} \hat{q}_+ + a_{p-} \hat{q}_- & \hat{q}_\varrho \sigma_s^0 + a_{+\psi} \hat{q}_+ + a_{-\psi} \hat{q}_- - (r\pi)^2 \end{bmatrix}}_{=\mathbf{G}_r} \begin{bmatrix} U_p \\ U_\psi \end{bmatrix}. \quad (\text{S-19})$$

The above system has non-trivial solution if $\det(\mathbf{G}_r) = 0$, which leads to a forth-order polynomial in $r\pi$

$$\ell_\kappa^2 (r\pi)^4 - 2 \left(\frac{\ell_\kappa^2 \mathbf{G}_0^{22} - \mathbf{G}_0^{11}}{2} \right) (r\pi)^2 - \det(\mathbf{G}_0) = 0. \quad (\text{S-20a})$$

We note that the entries of the matrix \mathbf{G}_0 are equivalent to those of the Hessian matrix of the free energy \tilde{F} associated with stationary problem describing non-linear localised solutions, see Eqs. (S-21) in the main text. This is not surprising since solving for the zeroth growth eigenmodes corresponds to solving the linearised stationary problem. The entries of the matrix \mathbf{G}_0 can then be easily computed as

$$\mathbf{G}_0^{22} = \tilde{F}_{\psi\psi}^0 = \frac{(q_p^0 \phi_p^0)^2}{(1 - \phi_p^0)} - \phi_+^0 - \phi_-^0 - q_s^0 \phi_s^0 - \phi_p^0 N \sigma_z^0, \quad (\text{S-20b})$$

$$\mathbf{G}_0^{11} = \tilde{F}_{\phi\phi}^0 = \frac{1}{N \phi_p^0} + \frac{(1 - \chi \phi_s^0)^2}{1 - \phi_p^0} - \chi^2 \phi_s^0, \quad (\text{S-20c})$$

$$\mathbf{G}_0^{12} = \mathbf{G}_0^{21} = \tilde{F}_{\psi\phi}^0 = \frac{q_p^0}{1 - \phi_p^0} (1 - \chi \phi_p^0 \phi_s^0) - \chi q_s^0 \phi_s^0. \quad (\text{S-20d})$$

We discussed the number and explicit form of the roots to Eq. (S-20) in Appendix B. Here, we focus instead on the connections between the roots to Eq. (S-20) and the temporal stability of homogeneous solutions. By continuity of the growth rate ω with respect to the model parameters, we know that changes in the temporal stability of a given mode r will imply r being a real root of Eq. (S-20). If Eq. (S-20) has no solution, then we expect all wavenumbers r to have the same stability properties. Based on the explicit computation of the dispersion relation (see Section III B), we know that the interval of unstable modes is bounded, which implies that if Eq. (S-20) has no solution then the homogeneous solutions are stable to all positive wavenumber r , *i.e.*, the growth rates ω associated with the eigenmode r are negative. When Eq. (S-20) has only two real roots, by symmetry, these are of the form $r = \pm r_1$. Following the same reasoning as above, we therefore conclude that the homogeneous state is temporally unstable to modes in the interval $r \in (0, r_1)$. Finally, if Eq. (S-20a) has four real eigenvalues, then these are of the form $r = \pm r_{1,2}$ with $r_1 > r_2$, and we expect the homogeneous solution to be unstable to perturbation of wavenumber in the interval $r \in (r_2, r_1)$. More details on the nature of transition in the temporal stability of homogeneous states are given in Appendix B.

SMIV. SPATIAL DYNAMICS.

In this section we detail the derivation of the system (14) that defines steady solution of Eqs. (S-2)-(S-5). For simplicity, we denote stationary solutions of the problem with capital letters, *i.e.*, $\Phi_m(x)$ and $\Psi(x)$ correspond, respectively, to the stationary spatial profile of the volume fraction for the component m of the mixture and the rescaled electric potential. To find the stationary solution, we set all time derivatives in Eq. (S-9) to zero. Because of the no-flux boundary condition and the 1D geometry, this is equivalent to setting the fluxes of each component of the mixture to zero. In line with the logarithmic form of the entropy of mixing, we here consider solutions with support on the whole domain $[0, L_\Omega]$, *i.e.*, $\Phi_m, q_s \in (0, 1)$ for all $x \in [0, L_\Omega]$. Under these assumptions, at steady state, Eq. (S-9c) enables to solve explicitly for the charge density q_s

$$q_s = \frac{e^{\mu_H^\Delta - \Psi}}{1 + e^{\mu_H^\Delta - \Psi}} = -\frac{\partial}{\partial \Psi} \left[\ln \left(1 + e^{\mu_H^\Delta - \Psi} \right) \right]$$

where μ_H^0 is an unknown constant characterising the equilibrium chemical potential of protons μ_H (see Eq. (S-3e)). Since q_s is a unique function of the electric field, the same holds for the mean charge on the polymer q_p

$$\mathcal{Z}_{\beta, Q}(\Psi) = \sum_{q=0}^{Q_p} e^{-\hat{u}_{\text{CR}, p}^q - q(\Psi - \mu_H^\Delta)}, \quad q_p = -\frac{1}{N} \frac{\partial \ln \mathcal{Z}_{\beta, Q}(\Psi)}{\partial \Psi},$$

where we have used Eq. (7) to write the moments of the mean charge q_p in terms of the partition function associated with the polymer charge distribution. We can further solve for the volume fractions of the salt ions Φ_\pm by considering a linear combination of zero flux conditions, namely $j_\pm \Phi_s - \Phi_\pm j_s = 0$ and coupling these with the no-void condition, we obtain

$$\begin{cases} \Phi_+(\Phi_p, \Psi) = \gamma_s(\Phi_p, \Psi) e^{-\Psi + \mu_+^\Delta + \chi \Phi_p} (1 - \Phi_p), \\ \Phi_-(\Phi_p, \Psi) = \gamma_s(\Phi_p, \Psi) e^{\Psi + \mu_-^\Delta + \chi \Phi_p} (1 - \Phi_p), \\ \Phi_s(\Phi_p, \Psi) = \gamma_s(\Phi_p, \Psi) \left(1 + e^{-\Psi + \mu_H^\Delta} \right) (1 - \Phi_p), \end{cases} \quad (\text{S-21})$$

where the constant μ_\pm^Δ are again unknown constants which specify the difference in chemical potential between each salt ion and the solvent, and γ_s is defined as

$$\gamma_s(\phi, \psi) = \frac{1}{1 + e^{-\psi + \mu_+^\Delta + \chi \phi} + e^{-\psi + \mu_H^\Delta} + e^{\psi + \mu_-^\Delta + \chi \phi}}. \quad (\text{S-22})$$

Substituting Eq. (S-21) into Eq. (S-2b), we find that the steady spatial profile for the electric potential Ψ is defined by

$$-\partial_{xx} \Psi = \frac{1 - \Phi_p}{\gamma_s(\Phi_p, \Psi)} \frac{\partial \gamma_s(\Phi_p, \Psi)}{\partial \Psi} - \frac{\Phi_p}{N} \frac{\partial \ln \mathcal{Z}_{\beta, Q}(\Psi)}{\partial \Psi}, \quad (\text{S-23})$$

Finally, the equation defining the steady spatial profiles for the polymer volume fraction Φ_p is obtained by considering the linear combination of the no-flux conditions $j_p \Phi_s - \Phi_p j_s = 0$, which leads to the following second-order differential

equation

$$\begin{aligned} \ell_\kappa^2 \partial_{xx} \Phi_p &= \frac{1}{N} \left[\ln \left(\frac{\Phi_p}{\mathcal{Z}_{\beta,Q}} \right) + 1 \right] - [\ln(\gamma_s(1 - \Phi_p)) + 1] + \chi \left((1 - \Phi_p) \gamma_s (1 + e^{\mu_H^\Delta - \Psi}) - \Phi_p \right) + \mu_p^\Delta \\ &= \frac{\partial}{\partial \Phi_p} \left[(1 - \Phi_p) \ln(\gamma_s(\Phi_p, \Psi)(1 - \Phi_p)) + \frac{\Phi_p}{N} \ln \left(\frac{\Phi_p}{\mathcal{Z}_{\beta,Q}(\Psi)} \right) + \chi \Phi_p (1 - \Phi_p) + \mu_p^\Delta \Phi_p \right], \end{aligned} \quad (\text{S-24})$$

where μ_p^Δ is an additional unknown constant that characterises the difference in the polymer and solvent chemical potentials at steady state. To obtain Eqs. (14) in Section III B 3 in the main text, we notice that the right-hand sides of Eqs. (S-23)-(S-24) can be written as the partial derivative of the rescaled free-energy:

$$\begin{aligned} \tilde{F} &= \hat{f}_{\text{eff}} + e\psi(q_s \Phi_s + q_p(q_s) \Phi_p - \Phi_- + \Phi_+) + \sum_{m \in \mathcal{I}_H \setminus \{s\}} \mu_m^\Delta \Phi_m \\ &= (1 - \Phi_p) \ln(\gamma_s(1 - \Phi_p)) + \frac{\Phi_p}{N} \ln(\gamma_p \Phi_p) + \chi \Phi_p (1 - \Phi_p), \end{aligned} \quad (\text{S-25})$$

where the activity coefficients γ_s and γ_p take the form:

$$\gamma_s = \frac{1}{1 + e^{-\psi + \mu_+^\Delta + \chi\phi} + e^{-\psi + \mu_H^\Delta} + e^{\psi + \mu_-^\Delta + \chi\phi}}, \quad (\text{S-26})$$

$$\gamma_p = \frac{e^{N\mu_p^\Delta}}{\mathcal{Z}_{\beta,Q}(\psi)} = \frac{e^{N\mu_p^\Delta}}{\sum_{q=0}^{Q_p} e^{-\beta u_{\text{CR}}^q - q(\psi - \mu_H^\Delta)}}. \quad (\text{S-27})$$

To uniquely identify the stationary solutions, it remains to specify the chemical potentials μ_m^Δ for $m \in \mathcal{I}_H \setminus \{s\}$. These four degrees of freedom are associated with mass conservation of ions, protons and polymers. One of these degrees of freedom is constrained by the overall electroneutrality of the mixture

$$\int_0^{\ell_\Omega} (q_s \Phi_s + q_p \Phi_p + \Phi_+ - \Phi_-) dx = 0.$$

We constrain the remaining three degrees of freedom by prescribing the spatially-averaged volume fraction of polymers, protons and positive salt ions:

$$\phi_p^0 = \frac{1}{\ell_\Omega} \int_0^{\ell_\Omega} \Phi_p(x) dx, \quad (\text{S-28a})$$

$$\phi_H^0 = \frac{1}{\ell_\Omega} \int_0^{\ell_\Omega} q_p(x) \Phi_p(x) + q_s(x) \Phi_s(x) dx, \quad (\text{S-28b})$$

$$\phi_+^0 = \frac{1}{\ell_\Omega} \int_0^{\ell_\Omega} \Phi_+(x) dx, \quad (\text{S-28c})$$

where ϕ_p^0 , ϕ_+^0 and ϕ_H^0 are arbitrary constant that parametrise the stationary solutions.

A similar formulation holds for the case of a polymer with fixed charge Q_p , except for the form of the γ_p term, which reduces to

$$\gamma_p = \exp[N\mu_p^\Delta + Q_p\psi]$$

and can take both values above and below one.

SMV. ADDITIONAL RESULTS: ENSEMBLE SIMULATIONS

A. Ensemble simulations

Here, we present additional results from numerical simulations of phase separation for different values of the average proton concentration c_H^0 . In Figure 3, we show the evolution of the polymer concentration for one specific noisy initial condition. To study how stable the long-term pattern is, we simulate the model for an ensemble of 50 noisy initial

conditions (for a fixed noise level of noise). To characterise the emergent pattern, we run the simulation up to a time $t = 1000T$ and then estimate the distribution of two metrics across the simulation ensemble: the average size of condensed micro-domains, and the number of liquid interfaces in the domain, which, when halved, gives a proxy for the number of coacervates. Results are illustrated in Figure SM1. We find that the variability in the number and size of condensed micro-domains is the largest in proton-dilute (c_H^0 very low) conditions, suggesting the pattern observed in the simulations is not robust to perturbations; in contrast, for medium levels of c_H^0 , we find minimal variations both in the number and size of the micro-domains suggesting the pattern is more stable than in dilute conditions and the characteristic length scale of the micro-domains is characteristic of the problem. This is in line with the linear stability and steady state analyses presented in Section IIIB.

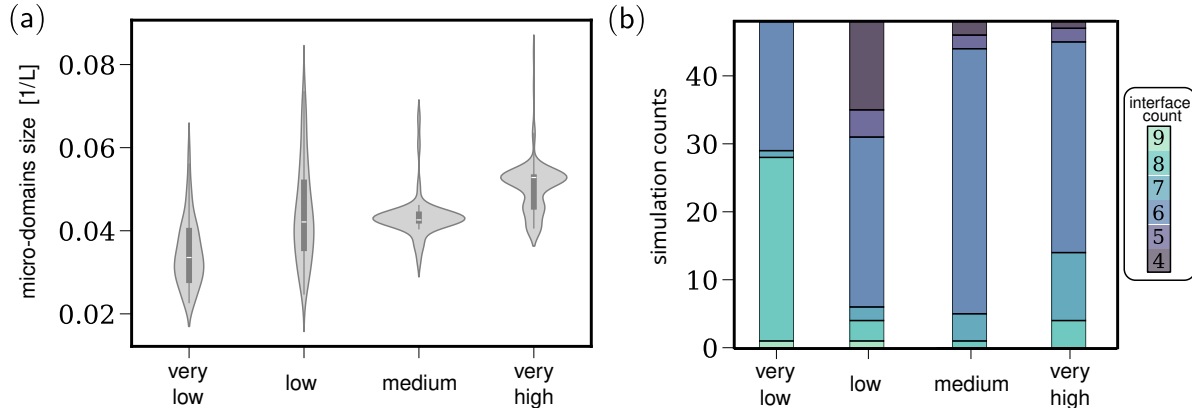


FIG. SM1: Plots quantifying the level of variability in the pattern emerging from ensemble simulations of spinoidal decomposition for different values of the average proton concentration c_H^0 . (a) Size distribution of the micro-domain size at simulation time $t = 1000T$; (b) Cumulative barplot illustrating the distribution of interface number at simulation time $t = 1000T$. The values of c_H^0 and all parameter are as in Figure 3.

B. Supplementary movie

Movie SM1. Initial transient dynamics, Ostwald ripening. Movie illustrating simulations of phase separation for an intermediate value of the c_H^0 (same as in Figure 2). We illustrate the time evolution of the local polymer number density c_p (see blue light blue curve) up to time $t = 15T$. Consecutive frames correspond to a time-step of $0.1T$. Model and scaling parameters are listed in Table SM1.

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