Electronic Appendix:

Kinetics of surface growth with coupled diffusion and the emergence of a universal growth path

---

Appendix A - Nomenclature

General framework:

$\mathcal{R}$	body manifold in the physical configuration
$\mathcal{R}^{\mathrm{R}}$	material manifold in the reference configuration
$\partial\mathcal{R}$	surface boundary of $\mathcal{R}$
$\partial\mathcal{R}^{\mathrm{R}}$	surface boundary of $\mathcal{R}^{\mathrm{R}}$
$\mathcal{S}_a$	association surface in the physical configuration
$\mathcal{S}_a^{\mathrm{R}}$	association surface in the reference configuration
$\mathcal{S}_d$	dissociation surface in the physical configuration
$\mathcal{S}_d^{\mathrm{R}}$	dissociation surface in the reference configuration
t	time variable
$\mathbf{y}$	spatial point in the physical configuration
$\mathbf{x}$	material point in the reference configuration
$\hat{\mathbf{y}}$	one on one mapping from reference configuration to physical configuration
$\hat{\mathbf{x}}$	inverse one on one mapping from physical configuration to reference configuration
$\mathbf{n}$	outward pointing normal vector on the boundary $\partial\mathcal{R}$ in the physical configuration
$\mathbf{n}^{\mathrm{R}}$	outward pointing normal vector on the boundary $\partial\mathcal{R}^{\mathrm{R}}$ in the reference configuration
$\mathrm{d}V_y$	volume element in the physical configuration
$\mathrm{d}V_x$	volume element in the reference configuration
$\mathrm{d}A_y$	area element in the physical configuration
$\mathrm{d}A_x$	area element in the reference configuration
$\mathbf{v}$	particle velocity in the physical configuration
$\mathbf{V}$	boundary velocity in the physical configuration
$\mathbf{V}_{\mathrm{G}}$	growth velocity in the physical configuration
$\mathbf{V}^{\mathrm{R}}$	boundary velocity in the reference configuration
$\mathbf{j}$	flux of solvent in the physical configuration
$\mathbf{j}^{\mathrm{R}}$	flux of solvent in the reference configuration
$\mathbf{F}$	deformation gradient
J	volume ratio
ϕ	physical volume fraction of solvent in the body
ϕ^{R}	referential volume fraction of solvent in the body
ψ	Helmholtz free energy of the body
ψ_e	Helmholtz elastic free energy associated with the solid matrix
ψ_s	Helmholtz free energy of the solvent
$\mathbf{T}$	Cauchy stress tensor
$\mathbf{S}$	Piola stress tensor
$\mathbf{b}$	body forces in the physical configuration
$\mathbf{b}^{\mathrm{R}}$	body forces in the reference configuration
p	hydrostatic pressure
μ	chemical potential of the solvent
f	driving force on the boundary
$\Delta\psi$	latent energy of growth
$\mathcal{G}$	growth function

Specific problem:

k	Boltzmann constant
T	temperature
N	number of polymer chains per unit volume
ν	volume of a solvent unit
χ	Flory-Huggins interaction parameter
D	diffusion coefficient
b	reaction constant
ψ_0	free energy of the unmixed solvent
ψ_a	potential energy gain at the association boundary
λ_0	imposed in-plane stretch

Appendix B - Rate of Change of Volume

Consider a material volume dV_x in the reference configuration, and let dV_y be the volume occupied by this same collection of particles in the current configuration. Recall that $dV_y = J dV_x$ where $J = \det \mathbf{F}$. The standard formula for differentiating the determinant reads

$$\frac{\mathrm{d}}{\mathrm{d}t}(\det \mathbf{F}) = (\det \mathbf{F})\ \mathrm{tr}\left(\frac{\mathrm{d}\mathbf{F}}{\mathrm{d}t}\mathbf{F}^{-1}\right), \tag{B1}$$

which can alternatively be written as

$$\dot{J} = J\ \mathrm{tr}\left(\dot{\mathbf{F}}\mathbf{F}^{-1}\right). \tag{B2}$$

Taking the derivative of $(2.3)^2$, we can write the relation $\dot{\mathbf{F}} = \mathrm{grad}\mathbf{v}\ \mathbf{F}$. Substituting the latter in (B2), we obtain the identity

$$\dot{J} = J\ \mathrm{div}\ \mathbf{v}. \tag{B3}$$

Appendix C - Explicit Formulae

In the following, we provide the full analytical formulae that have been represented in condensed form in the main text.

The continuity of the chemical potential (6.19) is

$$\ln\left(1-\frac{1}{J_d}\right)+\frac{1}{J_d}+\frac{\chi}{J_d^2}+N\nu\left(\frac{J_d}{\lambda_0^4}-\frac{1}{J_d}\right)=0. \tag{C1}$$

Equation (6.16) that relates the driving force to the swelling ratio can be further developed using (5.1)-(5.3), (5.8), (5.9) and (6.29) to write the driving force at the association boundary as

$$\begin{aligned} f_a(J_a) = \psi_0 + \psi_a - \frac{kT}{\nu}(J_a-1)\left[\ln\left(1-\frac{1}{J_a}\right)+\frac{\chi}{J_a}\right] - \frac{NkT}{2}\left(\frac{{J_a}^2}{\lambda_0^4}+2\lambda_0^2-3-2\ln J_a\right) \\ + \left\{\frac{kT}{\nu}\left[\ln\left(1-\frac{1}{J_a}\right)+\frac{1}{J_a}+\frac{\chi}{{J_a}^2}\right]+NkT\left(\frac{J_a}{\lambda_0^4}-\frac{1}{J_a}\right)\right\}J_a, \end{aligned} \tag{C2}$$

and at the dissociation boundary as

$$f_d(J_d) = \psi_0(1+J_d) - \frac{kT}{\nu}(J_d-1)\left[\ln\left(1-\frac{1}{J_d}\right)+\frac{\chi}{J_d}\right] - \frac{NkT}{2}\left(\frac{J_d^2}{\lambda_0^4}+2\lambda_0^2-3-2\ln J_d\right). \tag{C3}$$

Substituting (5.10) and (6.30) in (6.45) and (6.46), we can write in the physical space

$$\begin{aligned} y(J) = \frac{\lambda_0^2 D}{b\sinh\left(\frac{\nu}{kT}f_a(J_a)\right)}\left\{\frac{N\nu}{\lambda_0^4}\left[\ln\left(\frac{J}{J_a}\right)+\frac{1}{J}-\frac{1}{J_a}\right]-\frac{N\nu}{2}\left(\frac{1}{J^2}-\frac{1}{J_a^2}\right)+\right. \\ \left.\frac{1}{3}(N\nu+2\chi-1)\left(\frac{1}{J^3}-\frac{1}{J_a^3}\right)-\frac{\chi}{2}\left(\frac{1}{J^4}-\frac{1}{J_a^4}\right)\right], \end{aligned} \tag{C4}$$

and in the reference space

$$X(J) = \frac{\lambda_0^4 D}{b \sinh\left(\frac{\nu}{kT} f_a(J_a)\right)} \left[\frac{N\nu}{\lambda_0^4} \left(-\frac{1}{J} + \frac{1}{J_a} + \frac{1}{2J^2} - \frac{1}{2J_a^2} \right) - \frac{N\nu}{3} \left(\frac{1}{J^3} - \frac{1}{J_a^3} \right) + \right.$$
$$\left. \frac{1}{4} (N\nu + 2\chi - 1) \left(\frac{1}{J^4} - \frac{1}{J_a^4} \right) - \frac{2\chi}{5} \left(\frac{1}{J^5} - \frac{1}{J_a^5} \right) \right]. \tag{C5}$$

Analytical expressions for (6.35) and (6.38) can be obtained by replacing J and J_a in (C4) and (C5) by $\tilde{J}$ and $\tilde{J}_a$. Notice that the determination of J_a is required to use the above relations. During the evolution along the universal path, the swelling ratio at the association boundary $J_a(t)$ can be determined using the implicit equation (6.48). The thicknesses ℓ and ℓ^{R} of the body in the physical and the reference spaces are obtained by evaluating (C4) and (C5) at $J = J_d$.

Appendix D - Supplementary Figures

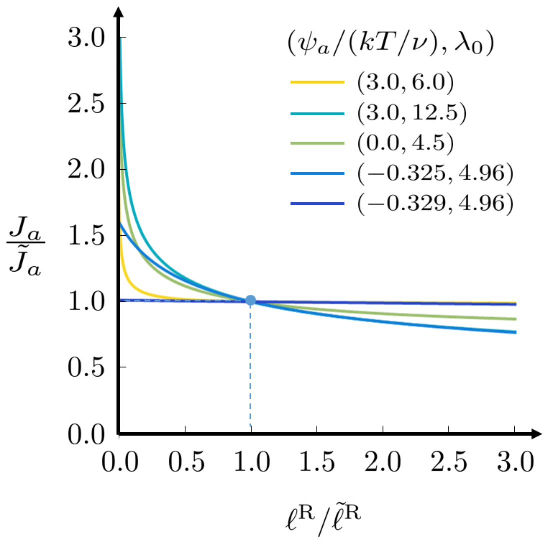

Figure D1: Effect of ψ_a and λ_0 on the universal path. The universal path determined by the numerical simulations is indistinguishable from that given by the analytical formula (6.46).

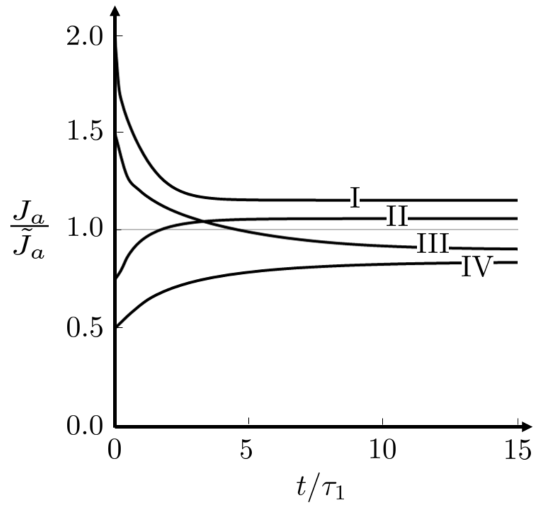

Figure D2: Time evolution of the swelling ratio $J_a(t) = J(y,t)|_{y=0}$ at the association boundary, during the diffusion-dominated stage for the four paths initiating in regions I-IV in Fig. 5. Time is normalized by $\tau_1 = 8.2 \times 10^3$s.

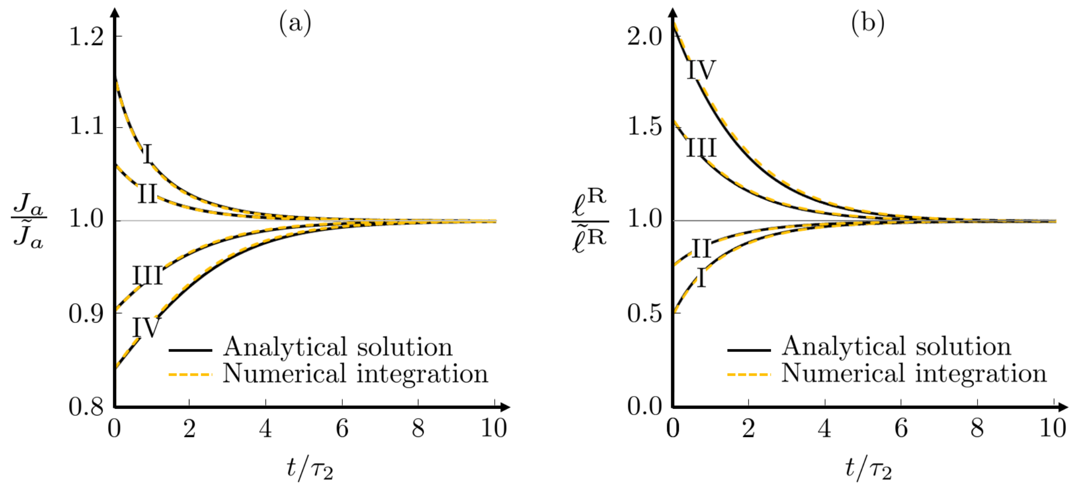

Figure D3: Time evolution of (a) the swelling ratio $J_a(t)$ and (b) the dry thickness $\ell^{\mathrm{R}}(t)$ at the association boundary along the universal path for the four initial conditions in regions I-IV shown in Fig. 5. Notice that time has been reset so that $t = 0$ corresponds to the time at which evolution along the universal path begins. The solid curves correspond to the analytical solution (6.48) and (6.46).