Journal Name

ARTICLE TYPE

Cite this: DOI: 00.0000/xxxxxxxxxx

Formation of glassy skins in drying polymer solutions: Approximate analytical solutions. Supplementary material

Laurence Talini,*[a] and François Lequeux[b]

Received Date
Accepted Date

DOI: 00.0000/xxxxxxxxxx

1 Numerical resolution

The resolution is done using the procedure *pdepe* of Matlab software, taking for the time mesh a quadratic interval with the i^{th} time variable equal to $t_i = i^2 t_{max}/N_t$ where t_{max} is the maximum time with i ranging from 0 to $N_t = 1000$. The spatial mesh is a mesh $x_j = 10^{12j/N_x - 8} - 10^{-8}$ with j ranging from 0 to $N_x = 1000$. These values ensure a good precision and stability for $n = 4$.

2 Approximate solution to the non-linear diffusion equation with a constant Ψ_s, and comparison with exact solution

When the surface value of Ψ is constant, the calculation is similar to the one of subsection 3.2. Eliminating J_{ev} between equations 29 and 32 of the main text yields

$$\frac{1}{2}\frac{d\xi^2}{dt} = D_0 \frac{\left[\int_{\Psi_s}^1 f(w)dw\right]^2}{\int_{\Psi_s}^1 (1-w)f(w)dw} \tag{1}$$

to which the solution is

$$\xi(t) = \left(\frac{2D_0 t}{\int_{\Psi_s}^1 (1-w)f(w)dw}\right)^{1/2} \int_{\Psi_s}^1 f(w)dw \tag{2}$$

The profile of Ψ is then obtained by using equation 14 of the main text. The exact solution is the solution to equation 10 of the main text, which can be numerically integrated. The exact and approximate solutions are displayed in figure 1.

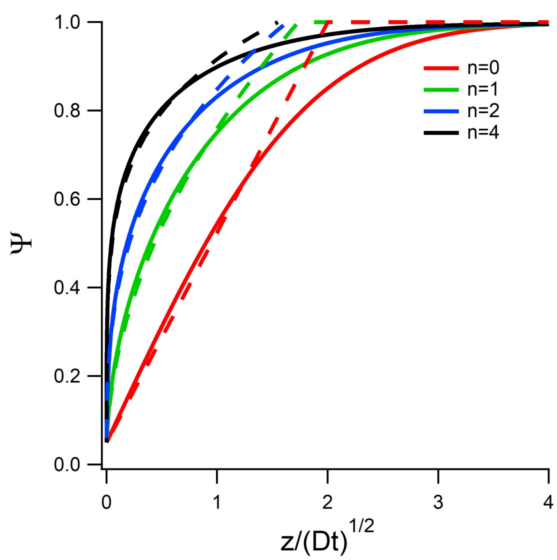

Fig. 1 Exact (full lines) and approximated (dashed lines) solutions for Ψ as a function of $\hat{z}$ with a constant value at the interface, $\Psi(0,t)$. The exact solutions are given by integration of equation 10 of the main text for different values of the exponent n characterising the decrease of the diffusion coefficient. The approximated solutions are given by equation 14 of the main text where the length ξ verifies equation 2.

[a] *CNRS, Surface du Verre et Interfaces, Saint-Gobain, Aubervilliers, France. E-mail: laurence.talini@cnrs.fr*
[b] *CNRS Sciences et Ingénierie de la Matière Molle, ESPCI Paris, PSL Research University, Sorbonne Université, Paris, France.*

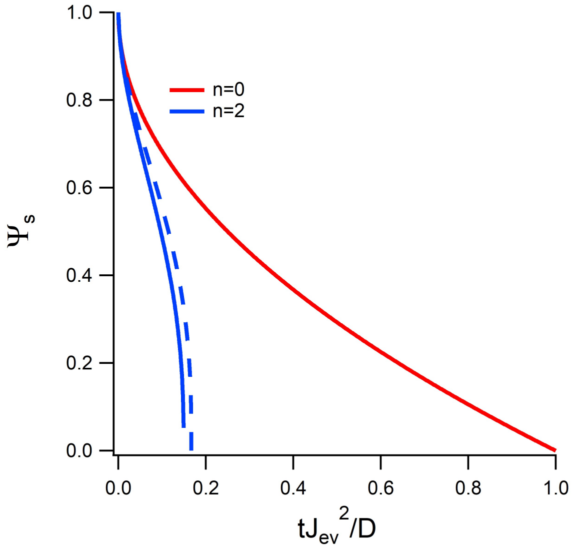

Fig. 2 Surface concentration as a function of the normalised time. The numerical resolutions of equation 10 of the main text (full lines) are shown for a constant diffusion coefficient (red) and an exponent $n = 2$ (blue). The dashed line corresponds to the approximation given by equation 4.

3 Approximate solution to the non-linear diffusion equation with a constant flux at the interface

In order to test once more our approximation, we consider a constant drying rate, for various singularities of D. We choose that D cancels for $\Psi = 0$ following relation 25 of the main text. Equation 29 of the main text yields

$$\xi(t) = \frac{D_0}{J_{ev}} \frac{1 - \Psi_s(t)^{n+1}}{n+1} \tag{3}$$

Because the flux is assumed to be constant, equation 32 of the main text can be integrated with respect to time, giving

$$J_{ev}t = \frac{D_0}{J_{ev}} \frac{1 + \Psi_s(t)^{n+1}[(n+1)\Psi_s - (n+2)]}{(n+1)(n+2)} \tag{4}$$

For $n = 0$, equations 3 and 4 lead to $\Psi_s(t) = 1 - J_{ev}\sqrt{\frac{2t}{D_0}}$ a result similar to equation 21 of the main text. We have compared the value of Ψ_s given by the approximation with the one that obtained by numerical resolution. The results are shown in figure 2. The approximation very satisfactorily predict the variation with time of the surface value of Ψ.

Notes and references