

# Tracking solvent diffusion in polymer microspheres - Supplementary information

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## SOLVENT TRANSPORT EQUATIONS

As discussed in the main text, we begin with the set of dimensional differential equations:

$$\frac{\partial U}{\partial t} = \frac{D}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial U}{\partial R} \right) \quad \text{for} \quad R_1(t) \leq R \leq R_2(t) \quad (1)$$

$$\frac{\partial U}{\partial t} = \frac{D_g}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial U}{\partial R} \right) \quad \text{for} \quad 0 \leq R < R_1(t) \quad (2)$$

$$U = U_0 > U^* \quad \text{at} \quad R = R_2(t) \quad (3)$$

$$D_g \frac{\partial U}{\partial R} \Big|_{R_1-\delta} - D \frac{\partial U}{\partial R} \Big|_{R_1+\delta} = (U - U^*) \frac{dR_1}{dt} \quad \text{at} \quad R = R_1(t) \quad (4)$$

$$\frac{dR_1}{dt} = -K(U - U^*)^\gamma \quad \text{at} \quad R = R_1(t) \quad (5)$$

$$\frac{dR_2}{dt} = \bar{\nu} D \frac{\partial U}{\partial R} + \bar{\nu} U_0 \frac{dR_2}{dt} - K_s \quad \text{at} \quad R = R_2(t). \quad (6)$$

where  $R_j(t)$  represents the position of the glass-rubber ( $j = 1$ ) and polymer swelling ( $j = 2$ ) interface at time  $t$  respectively,  $R$  is the radial coordinate,  $U = U(R, t)$  is the solvent concentration ( $\text{mol}/\text{m}^3$ ),  $D$  ( $D_g$ ) is the diffusion coefficient of the solvent ( $\text{m}^2/\text{s}$ ) in the rubber (glassy) region,  $U_0$  is the solubility of the solvent in the polymer ( $\text{mol}/\text{m}^3$ ),  $U^*$  is the threshold concentration required to initiate the glass-rubber transition ( $\text{mol}/\text{m}^3$ ),  $\delta$  is infinitesimally small,  $K$  is the kinetic parameter ( $\text{m}^{3\gamma+1}/(\text{s mol}^\gamma)$ ),  $\gamma$  is the nonlinear coefficient,  $\bar{\nu}$  is molar volume of the solvent ( $\text{m}^3/\text{mol}$ ) and  $K_s$  is the surface normalised erosion coefficient ( $\text{m}/\text{s}$ ).

Upon making an adiabatic approximation we decouple the diffusion problems in the glass and rubbery regions, as discussed in the main text. Denoting the typical length scale of the Fickian precursor in the glassy region as  $L$ , we consider the case when  $L \ll R_0$ , such that we can approximate the solvent concentration in the glassy region as  $U \approx U^* \exp[-(R - R_1)D_g^{-1}dR_1/dt]$ . Accordingly Eq. (4) transforms to read

$$D \frac{\partial U}{\partial R} = -U \frac{dR_1}{dt} \quad \text{at} \quad R = R_1(t). \quad (7)$$

Introducing the non-dimensional quantities

$$\tau = \frac{Dt}{R_0^2}, \quad \rho = \frac{R}{R_0}, \quad u(\rho, \tau) = \frac{U(R, T) - U^*}{U_0 - U^*} \quad (8)$$

$$\kappa = \frac{K_s R_0}{D}, \quad \rho_j(\tau) = \frac{R_j(t)}{R_0}, \quad \nu = \bar{\nu} U_0 \quad (9)$$

and the additional parameters

$$\mu = \frac{D}{K R_0} \frac{1}{(U_0 - U^*)^\gamma} \quad \text{and} \quad \sigma = \frac{U^*}{U_0 - U^*}, \quad (10)$$

Eqs. (1)–(7) can be transformed to read

$$\frac{\partial u}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left( \rho^2 \frac{\partial u}{\partial \rho} \right) \quad \text{for} \quad \rho_1(\tau) \leq \rho \leq \rho_2(\tau) \quad (11)$$

$$u = 1 \quad \text{at} \quad \rho = \rho_2(\tau) \quad (12)$$

$$\frac{\partial u}{\partial \rho} = -(u + \sigma) \frac{d\rho_1}{d\tau} \quad \text{at} \quad \rho = \rho_1(\tau) \quad (13)$$

$$u^\gamma = -\mu \frac{d\rho_1}{d\tau} \quad \text{at} \quad \rho = \rho_1(\tau) \quad (14)$$

$$\frac{d\rho_2}{d\tau} = \nu \frac{d\rho_2}{d\tau} + \frac{\nu}{1 + \sigma} \frac{\partial u}{\partial \rho} - \kappa \quad \text{at} \quad \rho = \rho_2(\tau). \quad (15)$$

The parameters  $\sigma$  and  $\mu$  are known as the Stefan number and non-dimensional kinetic parameter respectively. The former describes the ratio of the threshold solvent concentration to the difference between the maximum and threshold solvent concentration (or the latent solvent concentration).

Once the glass-rubber interface reaches the center of the sphere, Eqs. (13) and (14) are no longer valid and must be modified. Instead, a zero flux condition must hold at the center of the sphere, such that Eqs. (11)–(15) are replaced with the system of equations:

$$\frac{\partial u}{\partial \tau} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left( \rho^2 \frac{\partial u}{\partial \rho} \right) \quad \text{for} \quad 0 \leq \rho \leq \rho_2(\tau) \quad (16)$$

$$u = 1 \quad \text{at} \quad \rho = \rho_2(\tau) \quad (17)$$

$$\frac{\partial u}{\partial \rho} = 0 \quad \text{at} \quad \rho = 0 \quad (18)$$

$$\frac{d\rho_2}{d\tau} = \nu \frac{d\rho_2}{d\tau} + \frac{\nu}{1 + \sigma} \frac{\partial u}{\partial \rho} - \kappa \quad \text{at} \quad \rho = \rho_2(\tau). \quad (19)$$

An analytic solution to Eqs. (11)–(15) and (16)–(19) is not known, and hence they must be solved numerically. This can be approached by first applying the front fixing transformation

$$w = \frac{\rho - \rho_1}{\rho_2 - \rho_1}, \quad (20)$$

whereby Eqs. (11)–(15) become

$$\begin{aligned} (\rho_2 - \rho_1)^2 [\rho_1 + (\rho_2 - \rho_1)w]^2 \frac{\partial u}{\partial \tau} &= \frac{\partial}{\partial w} \left( [\rho_1 + (\rho_2 - \rho_1)w]^2 \frac{\partial u}{\partial w} \right) \\ &\quad - (\rho_2 - \rho_1)^2 [\rho_1 + (\rho_2 - \rho_1)w]^2 \frac{\partial u}{\partial w} \left[ \frac{w-1}{\rho_2 - \rho_1} \frac{d\rho_1}{dt} - \frac{w}{\rho_2 - \rho_1} \frac{d\rho_2}{dt} \right] \end{aligned} \quad \text{for} \quad 0 \leq w \leq 1 \quad (21)$$

$$u = 1 \quad \text{at} \quad w = 1 \quad (22)$$

$$\frac{\partial u}{\partial w} = -(u + \sigma)(\rho_2 - \rho_1) \frac{d\rho_1}{d\tau} \quad \text{at} \quad w = 0 \quad (23)$$

$$u^\gamma = -\mu \frac{d\rho_1}{d\tau} \quad \text{at} \quad w = 0 \quad (24)$$

$$\frac{d\rho_2}{d\tau} = \nu \frac{d\rho_2}{d\tau} + \frac{\nu}{(1 + \sigma)(\rho_2 - \rho_1)} \frac{\partial u}{\partial w} - \kappa \quad \text{at} \quad w = 1. \quad (25)$$

Once the glass-rubber interface has reached the center of the sphere Eqs. (23) and (24) are replaced with the zero flux condition

$$\frac{\partial u}{\partial w} = 0 \quad \text{at} \quad w = 0. \quad (26)$$

Numerical solution was then performed by applying the method of lines to the resulting equations and subsequently employing finite difference methods.

### Small time asymptotics

Utilising asymptotic expansions of  $u$ ,  $\rho_2$  and  $d\rho_1/d\tau$ , the small time behaviour of solvent concentration and boundary positions can be investigated. We are here only interested in the latter. The importance of such studies is twofold: firstly small time solutions act as initial seeds for the numerical solutions to the differential equations presented above, but also provide physical insight into the diffusion process. The derivation is lengthy and tedious and hence only the final results are presented here. Full details can, however, be found in [1]. Explicitly, we have for small times

$$\rho_1(\tau) \approx 1 - \frac{1}{\mu}\tau + \frac{n(1+\sigma)(1+h_1)}{2\mu^3}\tau^2 + \dots \quad (27)$$

$$\rho_2(\tau) \approx 1 + \frac{h_1}{\mu}\tau - \left( \frac{n(1+\sigma)h_1(1+h_1)}{2\mu^3} - \frac{h_2}{\mu^2} \right) \tau^2 + \dots \quad (28)$$

where

$$h_1 = \frac{\nu}{1-\nu} - \frac{\mu\kappa}{1-\nu}, \quad (29)$$

$$h_2 = -\frac{\nu[1+2\mu(1-\nu)]}{2\mu(1-\nu)^3} + \frac{\mu\{(1-\nu)[1+n(1+\sigma)]-1\}\kappa^2}{2(1-\nu)^3} + \frac{\{2-[n(1+\sigma)+2-2\mu](1-\nu)-2\mu(1-\nu)^2\}\kappa}{2(1-\nu)^3}. \quad (30)$$

These small time expressions are valid for times  $\tau = O(\mu^2)$  and exhibit non-Fickian or Case II type diffusion behaviour [1].

### Approximate solutions for $\sigma \ll 1$ , $\mu \gg 1$

Approximate solutions to Eqs. (11)–(15) can be found under various conditions, such as the small time limit described above. Derivation in the large Stefan number limit  $\sigma \gg 1$  is given in, for example, [2], however, for the systems considered in this work we find  $\sigma \ll 1$  and  $\mu \gtrsim 1$  such that we seek alternative expressions. We begin by considering the form of the solution of Eq. (11) under these conditions. Neglecting swelling temporarily for simplicity, we reformulate Eq. (11), by considering  $\tau = \tau(\rho_1)$ , such that we have

$$\frac{d\rho_1}{d\tau} \frac{\partial u}{\partial \rho_1} = \frac{1}{\rho^2} \frac{\partial}{\partial \rho} \left( \rho^2 \frac{\partial u}{\partial \rho} \right). \quad (31)$$

From Eq. (27) we note that at small times  $d\rho_1/d\tau \approx -1/\mu$ . For  $\mu \gg 1$  it is therefore natural to expand  $u$  in powers of  $1/\mu$ . Further asserting  $\sigma \ll 1$  we may write

$$u = u_{0,0} + \frac{1}{\mu}u_{1,0} + \sigma u_{0,1} + \frac{\sigma}{\mu}u_{1,1} + \frac{1}{\mu^2}u_{2,0} + \sigma^2 u_{0,2} + \dots \quad (32)$$

Substitution of Eq. (32) into Eqs. (11)–(15), yields a new set of differential equations, which to leading order read:

$$\frac{\partial^2 u_0}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial u_0}{\partial \rho} = 0 \quad \text{for} \quad \rho_1(\tau) \leq \rho \leq \rho_2(\tau) \quad (33)$$

$$u_0 = 1 \quad \text{at} \quad \rho = \rho_2(\tau) \quad (34)$$

$$\frac{\partial u_0}{\partial \rho} = -u_0 \frac{d\rho_1}{d\tau} \quad \text{at} \quad \rho = \rho_1(\tau) \quad (35)$$

$$u_0 = -\mu \frac{d\rho_1}{d\tau} \quad \text{at} \quad \rho = \rho_1(\tau) \quad (36)$$

$$\frac{1-\nu}{\nu} \frac{d\rho_2}{d\tau} = \frac{\partial u_0}{\partial \rho} \quad \text{at} \quad \rho = \rho_2(\tau). \quad (37)$$

$$(38)$$

Noting the solution

$$u_0 = 1 + A \left[ \frac{1}{\rho} - \frac{1}{\rho_2} \right] \quad (39)$$

automatically satisfies Eqs. (33) and (34), we can use Eqs. (35)–(37) to eliminate  $A$  yielding two further differential equations for  $\rho_1$  and  $\rho_2$  which read:

$$\mu \frac{d\rho_1}{d\tau} \left[ \frac{d\rho_1}{d\tau} \rho_1 (\rho_1 - \rho_2) + \rho_2 \right] + \rho_2 = 0 \quad (40)$$

$$\frac{1 - \nu}{3\nu\mu} \frac{d\rho_2^3}{d\tau} - \rho_1^2 \left( \frac{d\rho_1}{d\tau} \right)^2 = 0. \quad (41)$$

Eq. (40) can be analytically solved under the approximation  $\rho_2 \approx 1$ , as holds for the low solubility systems considered here, ultimately giving the parametric equation

$$\tau = \frac{1}{8} \sqrt{\frac{\mu}{\rho_2}} \left[ 4(1 - \rho_1) \sqrt{\mu\rho_2} + (\rho_2 - 2\rho_1) \sqrt{\mu\rho_2 + 4\rho_1(\rho_2 - \rho_1)} - (\rho_2 - 2) \sqrt{(\mu + 4)\rho_2 - 4} \right. \\ \left. + \rho_2(\mu + \rho_2) \left( \arctan \left[ \frac{\rho_2 - 2\rho_1}{\sqrt{\mu\rho_2 + 4\rho_1(\rho_2 - \rho_1)}} \right] - \arctan \left[ \frac{\rho_2 - 2}{\sqrt{(\mu + 4)\rho_2 - 4}} \right] \right) \right]. \quad (42)$$

Substituting Eq. (42) into (41) and solving gives the evolution of the outer sphere radius according to

$$\rho_2^3 = 1 + \frac{6\nu}{\nu - 1} \int_0^\tau \frac{\rho_1^2}{\mu + 2\rho_1 - 2\rho_1^2 + \sqrt{\mu^2 + 4\mu(\rho_1 - \rho_1^2)}} d\tau' \quad (43)$$

which must be evaluated numerically. Letting  $\rho_1 = 0$  and  $\rho_2 = 1$  in Eq. (42), allows the approximate time,  $\tau_f$  at which the glass-rubber interface reaches the center of the microsphere to be determined viz.

$$\tau_f \approx \frac{1}{4} [3\mu + \sqrt{\mu}(1 + \mu) \operatorname{arccot} \sqrt{\mu}]. \quad (44)$$

## OPTICAL WHISPERING GALLERY MODE RESONANCES

### Resonance shift for thick layers

In this Section we consider the derivation of Eqs. (10)–(11) of the main text, which describes the resonance shift of a spherical cavity due to an embedded layer of differing refractive index. We consider the geometry in Figure 1 which depicts a sphere of initial radius  $a$  and refractive index  $n_2$  immersed in a host medium of refractive index  $n_1$ , into which a layer of refractive index  $n_3$  and thickness  $T = a - b$  is introduced. Furthermore, we restrict our attention to the case when  $n_3 \approx n_2$ , i.e. to small refractive index differences. Using perturbation theory it has been shown [3] that the shift in resonance frequency,  $\omega$ , due to the layer is given by

$$\frac{\delta\omega}{\omega} \approx -\frac{1}{2} (\epsilon_3 - \epsilon_2) \frac{\int_{V_l} \mathbf{E}^\dagger(\mathbf{r}) \cdot \mathbf{E}'(\mathbf{r}) d\mathbf{r}}{\int_V \epsilon(\mathbf{r}) |\mathbf{E}(\mathbf{r})|^2 d\mathbf{r}} \quad (45)$$

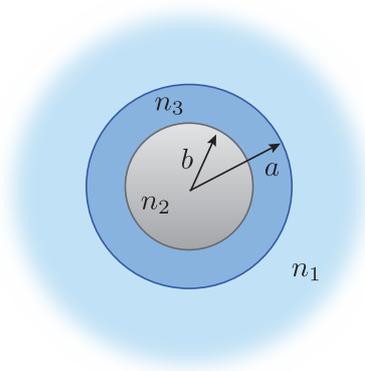


FIG. 1: Geometry of a layered sphere.

where  $\mathbf{E}(\mathbf{r})$  and  $\mathbf{E}'(\mathbf{r})$  denote the unperturbed and perturbed mode profile respectively,  $\epsilon_j = n_j^2$  is the relative permittivity of each medium,  $\epsilon(\mathbf{r})$  is the unperturbed permittivity distribution, such that  $\epsilon(\mathbf{r}) = n_1^2$  for  $r > a$  and  $n_2^2$  for  $r \leq a$ ,  $V_l$  denotes the volume of the layer and  $V$  denotes all space. For the unperturbed sphere, the field distribution for a single resonant mode of order  $(l, m)$  and polarisation index  $\nu$  ( $=$  TE or TM for transverse electric and magnetic modes respectively) is given by

$$\mathbf{E}(\mathbf{r}) = \begin{cases} b_{lm} \mathbf{E}_{lm}^{\nu(1)}(n_1, \mathbf{r}) & \text{for } r > a \\ c_{lm} \mathbf{E}_{lm}^{\nu(3)}(n_2, \mathbf{r}) & \text{for } r \leq a \end{cases} \quad (46)$$

where in spherical polar field components  $(E_r, E_\theta, E_\phi)$

$$\mathbf{E}_{lm}^{\text{TM}(s)}(n, \mathbf{r}) = \begin{bmatrix} l(l+1) \frac{h_l^{(s)}(nkr)}{r} Y_{lm}(\theta, \phi) \\ \frac{1}{r} \frac{d}{dr} (r h_l^{(s)}(nkr)) \frac{\partial}{\partial \theta} Y_{lm}(\theta, \phi) \\ \frac{im}{r \sin \theta} \frac{d}{dr} (r h_l^{(s)}(nkr)) Y_{lm}(\theta, \phi) \end{bmatrix} \quad (47)$$

$$\mathbf{E}_{lm}^{\text{TE}(s)}(n, \mathbf{r}) = \begin{bmatrix} 0 \\ \frac{-\omega \mu_0 m}{\sin \theta} h_l^{(s)}(nkr) Y_{lm}(\theta, \phi) \\ -i\omega \mu_0 h_l^{(s)}(nkr) \frac{\partial}{\partial \theta} Y_{lm}(\theta, \phi) \end{bmatrix}, \quad (48)$$

$k = \omega/c$  is the wavenumber,  $c$  is the speed of light in vacuum,  $\mu_0$  is the permeability of free space (non-magnetic media are assumed throughout this work),  $h_l^{(1)}(z)$  and  $h_l^{(2)}(z)$  are spherical Hankel functions of the first and second kind,  $h_l^{(3)}(z) = j_l(z)$  denotes the spherical Bessel function and  $h_l^{(4)}(z) = y_l(z)$  denotes the spherical Neumann function.  $Y_{lm}(\theta, \phi) = C_{lm} P_l^m(\cos \theta) \exp[im\phi]$  are the usual spherical harmonic functions,  $C_{lm} = [(2l+1)(l-|m|)!]^{1/2}/[4\pi(l+|m|)!]^{1/2}$  and  $P_l^m(\cos \theta)$  are the associated Legendre polynomials.

Without loss of generality we may adopt a mode normalisation such that  $c_{lm} = 1$ . The coefficient  $b_{lm}$  can be found by standard Mie theory, but is unneeded here. Upon introduction of the layer, the mode is perturbed such that

$$\mathbf{E}(\mathbf{r}) = \begin{cases} b'_{lm} \mathbf{E}_{lm}^{\nu(1)}(n_1, \mathbf{r}) & \text{for } r > a \\ c'_{lm} \mathbf{E}_{lm}^{\nu(3)}(n_2, \mathbf{r}) & \text{for } r \leq b \\ d'_{lm} \mathbf{E}_{lm}^{\nu(1)}(n_3, \mathbf{r}) + e'_{lm} \mathbf{E}_{lm}^{\nu(2)}(n_3, \mathbf{r}) & \text{for } b < r \leq a \end{cases}. \quad (49)$$

For small changes in refractive index, we may make the approximation  $c_{lm} \approx c'_{lm}$ , that is to say the mode within the central core is unperturbed, whereby it follows that  $d'_{lm} = \mu_l^\nu$ ,  $e'_{lm} = \tau_l^\nu$ , where

$$\mu_l^\nu = i \frac{n_3 k b}{2\sigma_{\nu 3}} \left[ \sigma_{\nu 2} h_l^{(3)}(n_2 k b) \psi_l^{(2)}(n_3 k b) - \sigma_{\nu 3} \psi_l^{(3)}(n_2 k b) h_l^{(2)}(n_3 k b) \right] \quad (50)$$

$$\tau_l^\nu = i \frac{n_3 k b}{2\sigma_{\nu 3}} \left[ \sigma_{\nu 3} h_l^{(1)}(n_3 k b) \psi_l^{(3)}(n_2 k b) - \sigma_{\nu 2} \psi_l^{(1)}(n_3 k b) h_l^{(3)}(n_2 k b) \right], \quad (51)$$

$\sigma_{\text{TM}j} = \epsilon_j$ ,  $\sigma_{\text{TE}j} = 1$  and  $\psi_l^{(s)}(z) = \frac{d}{dz} [z h_l^{(s)}(z)]$ . Noting that expressions for the denominator of Eq. (45) have been given previously in [4], evaluation of the resonance shift only requires determination of the numerator. Specifically, the integral can be written in the form

$$\int_{V_l} \mathbf{E}^\dagger(\mathbf{r}) \cdot \mathbf{E}'(\mathbf{r}) d\mathbf{r} = (\mu_l^\nu + \tau_l^\nu) \int_{V_l} \mathbf{E}_{lm}^{\nu(3)\dagger}(n_2, \mathbf{r}) \cdot \mathbf{E}_{lm}^{\nu(3)}(n_3, \mathbf{r}) d\mathbf{r} + i(\mu_l^\nu - \tau_l^\nu) \int_{V_l} \mathbf{E}_{lm}^{\nu(3)\dagger}(n_2, \mathbf{r}) \cdot \mathbf{E}_{lm}^{\nu(4)}(n_3, \mathbf{r}) d\mathbf{r}. \quad (52)$$

where we have used the relations  $h_l^{(1)}(z) = j_l(z) + iy_l(z)$  and  $h_l^{(2)}(z) = j_l(z) - iy_l(z)$ . Since we assume  $\delta n/n_2 \ll 1$  we also expand the prefactors of Eq. (52) around  $n_2$  yielding  $\mu_l^\nu + \tau_l^\nu = 1 + O(\delta n/n_2)$  and  $\mu_l^\nu - \tau_l^\nu = O(\delta n/n_2)$ . Furthermore, the angular integrals in Eq. (52) can be easily evaluated using the result

$$\int_0^\pi \left[ \frac{m^2}{\sin^2 \theta} P_l^m(\cos \theta)^2 + \left( \frac{d}{d\theta} P_l^m(\cos \theta) \right)^2 \right] \sin \theta d\theta = \frac{l(l+1)}{2\pi C_{lm}^2}, \quad (53)$$

such that we now need only consider the integrals

$$\mathcal{I}_s^{\text{TE}} = \int_b^a r^2 j_l(n_2kr) h_l^{(s)}(n_3kr) dr \quad (54)$$

$$\mathcal{I}_s^{\text{TM}} = \int_b^a l(l+1) \left( j_l(n_2kr) h_l^{(s)}(n_3kr) + \frac{d}{dr} [r j_l(n_2kr)] \frac{d}{dr} [r h_l^{(s)}(n_3kr)] \right) dr \quad (55)$$

$$= \frac{n_2^2 k^2}{2l+1} \left[ (l+1) \int_b^a r^2 j_{l-1}(n_2kr) h_{l-1}^{(s)}(n_3kr) dr + l \int_b^a r^2 j_{l+1}(n_2kr) h_{l+1}^{(s)}(n_3kr) dr \right] \quad (56)$$

where the latter equality for the TM case follows from the recursion relations for the spherical Bessel and Neumann functions [5]. These integrals can be evaluated analytically and are given by

$$\mathcal{I}_s^{\text{TE}} = \mathcal{F}_s^0(a) - \mathcal{F}_s^0(b) \quad (57)$$

$$\mathcal{I}_s^{\text{TM}} = \frac{n_2^2 k^2}{2l+1} [(l+1) [\mathcal{F}_s^-(a) - \mathcal{F}_s^-(b)] + l [\mathcal{F}_s^+(a) - \mathcal{F}_s^+(b)]] \quad (58)$$

with

$$\mathcal{F}_s^0(x) = x^2 \frac{j_l(n_2kx) h_l^{(s)}(n_3kx)}{(n_2^2 - n_3^2)k} \left[ \pm n_2 \frac{j_{l\pm 1}(n_2kx)}{j_l(n_2kx)} \mp n_3 \frac{h_{l\pm 1}^{(s)}(n_3kx)}{h_l^{(s)}(n_3kx)} \right] \quad (59)$$

$$\mathcal{F}_s^\pm(x) = x^2 \frac{j_l(n_2kx) h_l^{(s)}(n_3kx)}{(n_2^2 - n_3^2)k} \left[ \pm n_3 \frac{j_{l\pm 1}(n_2kx)}{j_l(n_2kx)} \mp n_2 \frac{h_{l\pm 1}^{(s)}(n_3kx)}{h_l^{(s)}(n_3kx)} \right] \quad (60)$$

where either the plus or minus sign can be taken for  $\mathcal{F}_s^0(x)$ .

## SIMULATION PARAMETERS

TABLE I: Simulation parameters found and derived from the literature

	PMMA - water	PS - water	Source(s)
Solvent density, $\rho_s$ (g cm <sup>-3</sup> )	1.000	1.000	[6]
Solvent molar weight, $\bar{m}$ (g mol <sup>-1</sup> )	18.0153	18.0153	[6]
Solvent molar volume, $\bar{v}$ (cm <sup>3</sup> mol <sup>-1</sup> )	18.0514	18.0514	[6]
Polymer density, $\rho_p$ (g cm <sup>-3</sup> )	1.185	1.050	[7]
Solvent refractive index, $n_s$	1.3238	1.3238	[8]
Polymer refractive index, $n_p$	1.4813	1.5718	[9]
Polymer absorption coefficient, $\alpha$ (m <sup>-1</sup> )	$\approx 55$	$\approx 51$	[10]
Diffusion coefficient, $D$ (cm <sup>2</sup> s <sup>-1</sup> )	$3.35 \times 10^{-8}$	$1.7 \times 10^{-7}$	[11, 12]
Equilibrium solvent concentration, $U_0$ (wt%)	1.5	0.8	[13, 14]
Glass transition temperature, $T_g$ (K)	380	368	[7]
Free-volume constant, $\alpha_f$ (K <sup>-1</sup> )	$3.2 \times 10^{-4}$	$3.7 \times 10^{-4}$	[15]
Polymer-penetrant parameter, $\beta$	$\approx 0.15$	$\approx 0.14$	[15]
Average penetrant front velocity, $\langle dR_1/dt \rangle$ (m s <sup>-1</sup> )	$\approx 10^{-7}$	$0.2 \times 10^{-10}$	[16–18]
Kinetic parameter, $K$ (m <sup>4</sup> s <sup>-1</sup> mol <sup>-1</sup> )	$2.646 \times 10^{-10}$	$1.597 \times 10^{-11}$	-
Molarity, $U_0$ (mol m <sup>-3</sup> )	986.392	466.079	-
Threshold concentration, $U^*$ (mol m <sup>-3</sup> )	115.320	107.815	-
Stefan number $\sigma$	0.1324	0.3009	-
Kinetic parameter $\mu$	0.2906	59.4204	-

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