Mathematical Model

The model described below is based on the work of Lu (2006) and Lu and Kim (2005) with our own understanding and some modifications. The mathematical model can be derived using the atomic flux and the driving force of diffusion. The atomic flux vector, $\vec{J} = J_1\vec{i} + J_2\vec{j}$, is defined as the amount of chemical species passing over unit length per unit time.

Deriving the Equations (One Dimensional Version):

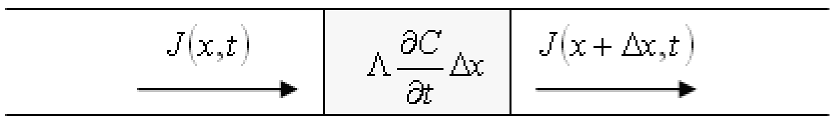

Figure 1: Derivation of one dimensional model

$J(x,t)$ is the amount of chemical species entering the shaded region per unit time and $J(x+\Delta x,t)$ is the amount of chemical species leaving the region per unit time. $\Lambda \frac{\partial C}{\partial t}\Delta x$ is the change in the number of moles of species accumulating (change in concentration) in this region per unit time, where Λ is the number of species per unit length. Thus, the amount of species entering the region minus the amount of species leaving the region is equal to the change in concentration per unit time. In mathematical terms, $J(x,t) - J(x+\Delta x,t) = \Lambda \frac{\partial C}{\partial t}\Delta x$. Bringing the Δx to the left side and taking the limit as $\Delta x \to 0$, we obtain $-\lim_{\Delta x \to 0} \frac{J(x+\Delta x,t) - J(x,t)}{\Delta x} = -\frac{\partial J}{\partial x} = \Lambda \frac{\partial C}{\partial t}$. Using Fick's diffusion law (Pelesko and Bernstein, 2003), which states that the atomic flux is negatively proportional the gradient of chemical potential (energy stored per mol of a species) per unit length, we can write the above equation as

$\Lambda \frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}\left(-M \frac{\partial \mu}{\partial x} \right) = M \frac{\partial^2 \mu}{\partial x^2}$, where M is the proportionality constant known as the diffusion coefficient, and μ is the chemical potential. This is the one dimensional model of our system and can be extended to two dimensions, which we are studying. The two dimensional derivation is similar but slightly more difficult, and we will not show it here. In the two dimensional model, $M \frac{\partial^2 \mu}{\partial x^2}$ becomes $M\nabla^2 \mu$ where $\nabla^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2}$. As demonstrated by Lu and Kim (2005), μ is defined as $\frac{1}{\Lambda}\left(\frac{\partial \bar{g}}{\partial C} + \frac{\partial f}{\partial C} \varepsilon_{\beta\beta} - 2h\nabla^2 C \right)$, where $\bar{g}$ is the excess energy created from the mixing of the chemical components (*see* Eq. 3), f $(= \psi + \phi C_1 + \eta C_2)$ is the surface stress (surface energy per unit of strain in the surface) assumed to be proportional to concentrations, $\varepsilon_{\beta\beta}$ is the strain in the surface, and h is a constant characterizing the contribution of chemical potential from phase boundaries. Since we are studying the patterns formed by two chemicals, the final set of equations is

$$\frac{\partial C_1}{\partial t} = \frac{M_1}{\Lambda^2} \nabla^2 \mu_1 = \frac{M_1}{\Lambda^2} \nabla^2 \left(\frac{\partial \bar{g}}{\partial C_1} + \frac{\partial f}{\partial C_1} \varepsilon_{\beta\beta} - 2h_1 \nabla^2 C_1 \right) \quad (1)$$

$$\frac{\partial C_2}{\partial t} = \frac{M_2}{\Lambda^2} \nabla^2 \mu_2 = \frac{M_2}{\Lambda^2} \nabla^2 \left(\frac{\partial \bar{g}}{\partial C_2} + \frac{\partial f}{\partial C_2} \varepsilon_{\beta\beta} - 2h_2 \nabla^2 C_2 \right) \quad (2)$$

where (Lu and Kim, 2005)

$$\begin{aligned} \bar{g}(C_1, C_2) = {} & \Lambda k_B T \left[C_1 \ln C_1 + C_2 \ln C_2 + (1 - C_1 - C_2) \ln (1 - C_1 - C_2) \right] + \\ & C_1 C_2 \left[\Omega_{12}^0 + \Omega_{12}^1 (C_1 - C_2) \right] + C_1 (1 - C_1 - C_2) \left[\Omega_{13}^0 + \Omega_{13}^1 (2C_1 + C_2 - 1) \right] + \\ & C_2 (1 - C_1 - C_2) \left[\Omega_{23}^0 + \Omega_{23}^1 (C_1 + 2C_2 - 1) \right] \end{aligned} \quad (3)$$

$$\varepsilon_{\beta\beta} = -\frac{(1-\nu^2)\phi}{\pi E} \iint \frac{(x_1 - \xi_1)\frac{\partial C_1}{\partial \xi_1} + (x_2 - \xi_2)\frac{\partial C_1}{\partial \xi_2}}{\left[(x_1 - \xi_1)^2 + (x_2 - \xi_2)^2 \right]^{3/2}} d\xi_1 d\xi_2 - \frac{(1-\nu^2)\eta}{\pi E} \iint \frac{(x_1 - \xi_1)\frac{\partial C_2}{\partial \xi_1} + (x_2 - \xi_2)\frac{\partial C_2}{\partial \xi_2}}{\left[(x_1 - \xi_1)^2 + (x_2 - \xi_2)^2 \right]^{3/2}} d\xi_1 d\xi_2 \quad (4)$$

C_1 — concentration of chemical component 1
C_2 — concentration of chemical component 2
μ_1 — chemical potential of component 1
μ_2 — chemical potential of component 2
M — diffusion coefficient
Λ — moles of component per area
$\bar{g}$ — excess energy created from the mixing of chemicals
k_B — Boltzmann's constant
Ω — bonding strength (subscript such as 12 means component 1 to component 2)
T — absolute temperature
f — surface stress due to concentration variations
$\varepsilon_{\beta\beta}$ — strain in the surface
h_1 and h_2 — constants characterizing chemical potential from phase boundaries
E — Young's modulus (stiffness of substrate)
v — Poisson's ratio of the substrate
ϕ — surface stress per mole of component 1
η — surface stress per mole of component 2

Scaled Equations:

We now scale the equations to reduce model parameters. The scaled equations are

$$\frac{\partial C_1}{\partial \tau} = \nabla^2 \left[P_1(C_1, C_2) - 2\nabla^2 C_1 + \varepsilon^*_1 \right] \tag{5}$$

$$\frac{\partial C_2}{\partial \tau} = S\nabla^2 \left[P_2(C_1, C_2) - 2H\nabla^2 C_2 + \varepsilon^*_2 \right] \tag{6}$$

where

$$\varepsilon^*_1 = -\frac{Q_1}{\pi} \iint \frac{(x_1-\xi_1)\frac{\partial C_1}{\partial \xi_1} + (x_2-\xi_2)\frac{\partial C_1}{\partial \xi_2}}{\left[(x_1-\xi_1)^2 + (x_2-\xi_2)^2\right]^{3/2}} d\xi_1 d\xi_2 - \frac{Q_2}{\pi} \iint \frac{(x_1-\xi_1)\frac{\partial C_2}{\partial \xi_1} + (x_2-\xi_2)\frac{\partial C_2}{\partial \xi_2}}{\left[(x_1-\xi_1)^2 + (x_2-\xi_2)^2\right]^{3/2}} d\xi_1 d\xi_2 \tag{7}$$

$$\varepsilon^*_2 = -\frac{Q_2}{\pi} \iint \frac{(x_1-\xi_1)\frac{\partial C_1}{\partial \xi_1} + (x_2-\xi_2)\frac{\partial C_1}{\partial \xi_2}}{\left[(x_1-\xi_1)^2 + (x_2-\xi_2)^2\right]^{3/2}} d\xi_1 d\xi_2 - \frac{Q_3}{\pi} \iint \frac{(x_1-\xi_1)\frac{\partial C_2}{\partial \xi_1} + (x_2-\xi_2)\frac{\partial C_2}{\partial \xi_2}}{\left[(x_1-\xi_1)^2 + (x_2-\xi_2)^2\right]^{3/2}} d\xi_1 d\xi_2 \tag{8}$$

$$\begin{aligned} P_1(C_1, C_2) = \frac{1}{\Lambda k_B T}\frac{\partial \bar{g}}{\partial C_1} = \ln\left(\frac{C_1}{1-C_1-C_2}\right) + C_2\left[\Omega_{12}^0 + \Omega_{12}^1 (C_1 - C_2)\right] - \\ C_2\left[\Omega_{23}^0 + \Omega_{23}^1 (C_1 + 3C_2 - 2)\right] + \Omega_{13}^0 (1 - 2C_1 - C_2) + \\ \Omega_{13}^1 (C_1 + 2C_2 - 6C_1^2 - C_2^2 - 6C_1 C_2 - 1) \end{aligned} \tag{9}$$

$$P_2(C_1,C_2) = \frac{1}{\Lambda k_B T}\frac{\partial \bar{g}}{\partial C_2} = \ln\left(\frac{C_2}{1-C_1-C_2}\right) + C_1\left[\Omega_{12}^0 + \Omega_{12}^1(C_1 - 2C_2)\right] -$$
$$C_1\left[\Omega_{13}^0 + \Omega_{13}^1(3C_1 + 2C_2 - 2)\right] + \Omega_{23}^0(1 - C_1 - 2C_2) +$$
$$\Omega_{13}^1(2C_1 + 6C_2 - C_1^2 - 6C_2^2 - 6C_1C_2 - 1) \quad (10)$$

$$Q_1 = \frac{b}{l_1}, \qquad Q_2 = \frac{b}{l_2}, \qquad Q_3 = \frac{b}{l_3} \quad (11)$$

$$S = \frac{M_2}{M_1}, \qquad H = \frac{h_2}{h_1} \quad (12)$$

$$l_1 = \frac{Eh_1}{(1-v^2)\phi^2}, \qquad l_2 = \frac{Eh_1}{(1-v^2)\phi\eta}, \qquad l_3 = \frac{Eh_1}{(1-v^2)\eta^2} \quad (13)$$

$$b = \sqrt{\frac{h_1}{\Lambda k_B T}} \quad (14)$$

$$\tau = \frac{h_1}{M_1(k_B T)^2} \quad (15)$$

Only the *Q*'s, *S*, and *H* after scaling need to be assigned values for simulations. Putting in additional parameters such as *E* will be unnecessary because we will eventually calculate *Q* anyways.

Adding Temperature Effects:

Eq. 5 and Eq. 6 assume a constant temperature. However, it is obvious that temperature fluctuations cause chemicals to behave differently. This is an important aspect that we plan to model, and these equations have to be modified to include temperature changes during a simulation. The terms we add in are based on experimental data and observations. According to

Anderson and Crerar (1993), $\bar{g}$ (*see* Eq. 3) is a linear function of temperature. First we change the equations slightly. In Eq. 3, instead of having T multiply to the entire equation, we only multiply it to the ideal mixing terms (the logarithmic terms). A new T_0 is introduced and is multiplied to the rest of the equation (the non-ideal mixing terms). We then multiply the terms containing Ω^0_{ab} and Ω^1_{ab} by $1+\alpha_{ab}(T_0 - T)$, where α_{ab} is a constant. For example, $C_1C_2\left[\Omega^0_{12} + \Omega^1_{12}(C_1 - C_2)\right]$ becomes $C_1C_2\left[\Omega^0_{12} + \Omega^1_{12}(C_1 - C_2)\right]\left[1+\alpha_{12}(T_0 - T)\right]$. The new $\bar{g}$ that incorporates temperature is

$$\begin{aligned}\bar{g}(C_1,C_2) = \Lambda k_B T_0 \Big\{ &\frac{T}{T_0}\left[C_1 \ln C_1 + C_2 \ln C_2 + (1 - C_1 - C_2)\ln(1 - C_1 - C_2)\right] + \\ &C_1C_2\left[\Omega^0_{12} + \Omega^1_{12}(C_1 - C_2)\right]\left[1+\alpha_{12}(T_0 - T)\right] + \\ &C_1(1 - C_1 - C_2)\left[\Omega^0_{13} + \Omega^1_{13}(2C_1 + C_2 - 1)\right]\left[1+\alpha_{13}(T_0 - T)\right] + \\ &C_2(1 - C_1 - C_2)\left[\Omega^0_{23} + \Omega^1_{23}(C_1 + 2C_2 - 1)\right]\left[1+\alpha_{23}(T_0 - T)\right]\Big\}\end{aligned} \tag{16}$$

Using this new equation, P_1 and P_2 (Eq. 9 and Eq. 10) become

$$\begin{aligned}P_1(C_1,C_2) &= \frac{1}{\Lambda k_B T_0}\frac{\partial \bar{g}}{\partial C_1} \\ &= \frac{T}{T_0}\ln\left(\frac{C_1}{1 - C_1 - C_2}\right) + C_2\left[\Omega^0_{12} + \Omega^1_{12}(2C_1 - C_2)\right]\left[1+\alpha_{12}(T_0 - T)\right] - \\ &\quad C_2\left[\Omega^0_{23} + \Omega^1_{23}(2C_1 + 3C_2 - 2)\right]\left[1+\alpha_{23}(T_0 - T)\right] + \\ &\quad \left[\Omega^0_{13}(1 - 2C_1 - C_2) + \Omega^1_{13}(6C_1 + 2C_2 - 6C_1^2 - C_2^2 - 6C_1C_2 - 1)\right]\left[1+\alpha_{13}(T_0 - T)\right]\end{aligned} \tag{17}$$

$$\begin{aligned}P_2(C_1,C_2) &= \frac{1}{\Lambda k_B T_0}\frac{\partial \bar{g}}{\partial C_2} \\ &= \frac{T}{T_0}\ln\left(\frac{C_2}{1 - C_1 - C_2}\right) + C_1\left[\Omega^0_{12} + \Omega^1_{12}(C_1 - 2C_2)\right]\left[1+\alpha_{12}(T_0 - T)\right] - \\ &\quad C_1\left[\Omega^0_{13} + \Omega^1_{13}(3C_1 + 2C_2 - 2)\right]\left[1+\alpha_{13}(T_0 - T)\right] + \\ &\quad \left[\Omega^0_{23}(1 - C_1 - 2C_2) + \Omega^1_{13}(2C_1 + 6C_2 - C_1^2 - 6C_2^2 - 6C_1C_2 - 1)\right]\left[1+\alpha_{13}(T_0 - T)\right]\end{aligned} \tag{18}$$

Temperature changes also affect the rate at which the chemicals diffuse; thus, M_1 and M_2 must be a function of temperature. According to experimental results (Kaganovskii et al., 1998), this rate increases exponentially with temperature. To capture this effect this, we multiply M_1 and M_2 by $e^{-\frac{\Delta E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)}$, where ΔE is the activation energy (kilojoules per mole) and R is the ideal gas constant (8.314 joules per mole Kelvin). The final modification we make is to Young's modulus E, the stiffness. The experimental results of Jeong et al. (2003) show that Young's modulus decreases linearly as temperature increases. So we multiply it by $1+\beta(T_0 - T)$. This constant divides all of the Q's after scaling. In general, after scaling and transforming, the temperature constants will remain unchanged.

Numerical Solution

The set of integral-differential equations Eq. 5 and Eq. 6 are impossible to solve analytically. However, we can use the Fourier Transform to simplify them enough so that they can be solved numerically using a semi-implicit method. First, initial and boundary conditions must be given in order to solve these equations. The initial condition is the beginning pattern created by the user. Two possible initial conditions are considered: homogeneous and heterogeneous (e.g. certain areas have higher concentrations). For boundary condition, we let both concentrations to be zero at infinity, that is, $\begin{matrix} C(-\infty, x_2, t) = 0, & C(\infty, x_2, t) = 0 \\ C(x_1, -\infty, t) = 0, & C(x_1, \infty, t) = 0 \end{matrix}$. This convention is useful when we transform the equations. In addition to these, we also let the successive derivatives (up to the third order) to be zero at infinity[1]. Again, these help in the Fourier transformations.

Let the Fourier Transformation be defined as

$$\hat{C}(k_1, k_2, t) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} C(x_1, x_2, t)\, e^{-i(k_1 x_1 + k_2 x_2)}\, dx_1 dx_2 \qquad (19)$$

The $\frac{1}{2\pi}$ can be included however it is unnecessary because it will eventually drop out and will only act as minor scaling factor if we do include it.

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[1] $\begin{matrix} \frac{\partial^n C}{\partial x_1^n}(-\infty, x_2, t) = 0, & \frac{\partial^n C}{\partial x_1^n}(\infty, x_2, t) = 0 \\ \frac{\partial^n C}{\partial x_2^n}(x_1, -\infty, t) = 0, & \frac{\partial^n C}{\partial x_2^n}(x_1, \infty, t) = 0 \\ n = 1,2,3 & \end{matrix}$

Transformation of the Time Derivative:

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\partial C}{\partial t}e^{-i(k_1x_1+k_2x_2)}dx_1dx_2=\frac{\partial}{\partial t}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}C(x_1,x_2,t)e^{-i(k_1x_1+k_2x_2)}dx_1dx_2=\frac{\partial \hat{C}}{\partial t} \qquad (20)$$

Transformation of the Laplacian:

$$\nabla^2 C=\frac{\partial^2 C}{\partial x_1^2}+\frac{\partial^2 C}{\partial x_2^2} \qquad (21)$$

We here only show the transformation of the first term since the transformation of the second one follows the same procedure.

$$\begin{aligned}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\partial^2 C}{\partial x_1^2}e^{-i(k_1x_1+k_2x_2)}dx_1dx_2 &= \int_{-\infty}^{\infty}\left[e^{-i(k_1x_1+k_2x_2)}\frac{\partial C}{\partial x_1}+ik_1\int\frac{\partial C}{\partial x_1}e^{-i(k_1x_1+k_2x_2)}dx_1\right]_{-\infty}^{\infty}dx_2\\ &= ik_1\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\partial C}{\partial x_1}e^{-i(k_1x_1+k_2x_2)}dx_1dx_2\\ &= ik_1\int_{-\infty}^{\infty}\left[e^{-i(k_1x_1+k_2x_2)}C(x_1,x_2,t)+ik_1\int C(x_1,x_2,t)e^{-i(k_1x_1+k_2x_2)}dx_1\right]_{-\infty}^{\infty}dx_2\\ &= -k_1^2\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}C(x_1,x_2,t)e^{-i(k_1x_1+k_2x_2)}dx_1dx_2\\ &= -k_1^2\hat{C}(k_1,k_2,t)\end{aligned} \qquad (22)$$

Here we use integration by parts[2] twice and the boundary conditions, which are $\left.e^{-i(k_1x_1+k_2x_2)}\frac{\partial C}{\partial x_1}\right|_{-\infty}^{\infty}=0$ and $\left[e^{-i(k_1x_1+k_2x_2)}C(x_1,x_2,t)\right]_{-\infty}^{\infty}=0$. Using a similar procedure, we can obtain the transformation of the second term, which is $-k_2^2\hat{C}(k_1,k_2,t)$. Adding these two transformations together, we have $\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\nabla^2 Ce^{-i(k_1x_1+k_2x_2)}dx_1dx_2=-k^2\hat{C}(k_1,k_2,t)$, where $k=\sqrt{k_1^2+k_2^2}$. Note that this procedure also applies to $P(x_1,x_2,t)$, which becomes

[2] $\int f(x)g'(x)dx=f(x)g(x)-\int f'(x)g(x)dx$

$-k^2\hat{P}(k_1,k_2,t)$. This method can be extended to any order derivative since it only requires integration by parts and the boundary conditions. Therefore, $\nabla^4 C$ becomes $k^4\hat{C}$).

Transformation of the Double Integration Term:

The transformation of the double integral terms in Eq. 7 and Eq. 8 is adopted from Hu et al. (2007). This transformation involves writing the double integral as a convolution and using the fact that the Fourier transformation of a convolution is the product of the Fourier transformation of each function[3] (Convolution Theorem).

$$\iint \frac{(x_1-\xi_1)\frac{\partial C}{\partial \xi_1} + (x_2-\xi_2)\frac{\partial C}{\partial \xi_2}}{\left[(x_1-\xi_1)^2+(x_2-\xi_2)^2\right]^{3/2}} d\xi_1 d\xi_2 = \iint \frac{(x_1-\xi_1)\frac{\partial C}{\partial \xi_1} d\xi_1 d\xi_2}{\left[(x_1-\xi_1)^2+(x_2-\xi_2)^2\right]^{3/2}} + \iint \frac{(x_2-\xi_2)\frac{\partial C}{\partial \xi_2} d\xi_1 d\xi_2}{\left[(x_1-\xi_1)^2+(x_2-\xi_2)^2\right]^{3/2}} \quad (23)$$

Again we here only show the transformation of the first term. Let $\rho = \left[(x_1-\xi_1)^2+(x_2-\xi_2)^2\right]^{-1/2}$. Taking the partial derivative of ρ with respect to ξ_1, we have $\frac{\partial \rho}{\partial \xi_1} = \frac{(x_1-\xi_1)}{\left[(x_1-\xi_1)^2+(x_2-\xi_2)^2\right]^{3/2}}$. Substituting it into the first term of Eq. 23, we obtain $\iint \frac{\partial \rho}{\partial \xi_1}\frac{\partial C}{\partial \xi_1} d\xi_1 d\xi_2$, which is the convolution of the partial derivatives of $\rho = (x_1^2+x_2^2)^{-1/2}$ and $C(x_1,x_2,t)$ (t is constant) with respect to x_1, or $\iint \frac{\partial \rho}{\partial \xi_1}\frac{\partial C}{\partial \xi_1} d\xi_1 d\xi_2 = -\frac{\partial \rho}{\partial x_1} * \frac{\partial C}{\partial x_1}$. Using the Convolution Theorem and the method for transforming spatial derivatives (previous transformation), we obtain

$$\begin{aligned} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\left(-\frac{\partial \rho}{\partial x_1} * \frac{\partial C}{\partial x_1}\right) e^{-i(k_1x_1+k_2x_2)} dx_1 dx_2 &= -\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\partial \rho}{\partial x_1} e^{-i(k_1x_1+k_2x_2)} dx_1 dx_2 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\frac{\partial C}{\partial x_1} e^{-i(k_1x_1+k_2x_2)} dx_1 dx_2 \\ &= -ik_1\hat{\rho}\cdot ik_1\hat{C} \\ &= k_1^2\hat{\rho}\hat{C} \end{aligned} \quad (24)$$

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[3] $F[f(x) * g(x)] = F[f(x)] \cdot F[g(x)]$

Similarly, the transformation of the second term is $k_2^2 \hat{\rho}\hat{C}$. Thus, the Fourier transformation of the double integral is the sum of the two individual transformations, or $k^2 \hat{\rho}\hat{C}$. It can be shown that $\hat{\rho} = \frac{2\pi}{k}$, which produces $2\pi k\hat{C}$. Finally, using the method for transforming the Laplacian, we obtain $-2\pi k^3 \hat{C}$.

In summary, we have

$$
\begin{aligned}
&\frac{\partial C}{\partial t} \Rightarrow \frac{\partial \hat{C}}{\partial t} \\
&\nabla^2 C \Rightarrow -k^2 \hat{C} \\
&\nabla^2 P \Rightarrow -k^2 \hat{P} \\
&\nabla^4 C \Rightarrow k^4 \hat{C} \\
&\iint \frac{(x_1-\xi_1)\frac{\partial C}{\partial \xi_1} + (x_2-\xi_2)\frac{\partial C}{\partial \xi_2}}{\left[(x_1-\xi_1)^2 + (x_2-\xi_2)^2\right]^{3/2}}\, d\xi_1 d\xi_2 \Rightarrow 2\pi k\hat{C} \\
&\nabla^2 \iint \frac{(x_1-\xi_1)\frac{\partial C}{\partial \xi_1} + (x_2-\xi_2)\frac{\partial C}{\partial \xi_2}}{\left[(x_1-\xi_1)^2 + (x_2-\xi_2)^2\right]^{3/2}}\, d\xi_1 d\xi_2 \Rightarrow -2\pi k^3\hat{C}
\end{aligned}
\tag{25}
$$

Consequently, Eq. 5 and Eq. 6 become

$$\frac{\partial \hat{C}_1}{\partial t} = -k^2 \hat{P}_1 - 2k^4 \hat{C}_1 + 2k^3 Q_1 \hat{C}_1 + 2k^3 Q_2 \hat{C}_2 \tag{26}$$

$$\frac{\partial \hat{C}_2}{\partial t} = S\left(k^2 \hat{P}_2 - 2k^4 H \hat{C}_2 + 2k^3 Q_2 \hat{C}_1 + 2k^3 Q_3 \hat{C}_2\right) \tag{27}$$

Semi-Implicit Method:

Eq. 26 and Eq. 27 can be solved using a semi-implicit method proposed by Chen and Shen (1998). This method treats the non-linear $\hat{P}$ terms explicitly and the linear $\hat{C}$ terms implicitly. First, let $\hat{P}^n = \hat{P}(k_1, k_2, t)$, $\hat{C}^n = \hat{C}(k_1, k_2, t)$, and $\hat{C}^{n+1} = \hat{C}(k_1, k_2, t+\Delta t)$ (with subscripts 1 and 2). Also, let $\frac{\partial \hat{C}}{\partial t} = \frac{\hat{C}^{n+1} - \hat{C}^n}{\Delta t}$ (also with subscripts). Eq. 26 and Eq. 27 become

$$\frac{\hat{C}_1^{n+1}-\hat{C}_1^{n}}{\Delta t} = -k^2\hat{P}_1^n - 2k^4\hat{C}_1^{n+1} + 2k^3Q_1\hat{C}_1^{n+1} + 2k^3Q_2\hat{C}_2^{n+1} \tag{28}$$

$$\frac{\hat{C}_2^{n+1}-\hat{C}_2^{n}}{\Delta t} = S\left(-k^2\hat{P}_2^n - 2k^4H\hat{C}_2^{n+1} + 2k^3Q_2\hat{C}_1^{n+1} + 2k^3Q_3\hat{C}_2^{n+1}\right) \tag{29}$$

In matrix form, these equations combine as

$$\frac{1}{\Delta t}\begin{Bmatrix}\hat{C}_1^{n+1}-\hat{C}_1^{n}\\ \hat{C}_2^{n+1}-\hat{C}_2^{n}\end{Bmatrix} = \begin{bmatrix}-2k^4+2k^3Q_1 & 2k^3Q_2\\ 2Sk^3Q_2 & -2SHk^4+2Sk^3Q_1\end{bmatrix}\times\begin{Bmatrix}\hat{C}_1^{n+1}\\ \hat{C}_2^{n+1}\end{Bmatrix} - k^2\begin{Bmatrix}\hat{P}_1^{n}\\ S\hat{P}_2^{n}\end{Bmatrix} \tag{30}$$

Solving for $\begin{Bmatrix}\hat{C}_1^{n+1}\\ \hat{C}_2^{n+1}\end{Bmatrix}$, we obtain

$$\begin{Bmatrix}\hat{C}_1^{n+1}\\ \hat{C}_2^{n+1}\end{Bmatrix} = \begin{bmatrix}1+\left(2k^4-2k^3Q_1\right)\Delta t & -2k^3Q_2\Delta t\\ -2Sk^3Q_2\Delta t & 1+S\left(2Hk^4-2k^3Q_3\right)\Delta t\end{bmatrix}^{-1}\times\left[\begin{Bmatrix}\hat{C}_1^{n}\\ \hat{C}_2^{n}\end{Bmatrix} - k^2\Delta t\begin{Bmatrix}\hat{P}_1^{n}\\ S\hat{P}_2^{n}\end{Bmatrix}\right] \tag{31}$$

Eq. 31 is in the form that can be implemented in a code. The inverse matrix can be found using a formula for 2x2 matrices[4]. With the temperature constants added in the previous section, Eq. 31 becomes (the key equation)

$$\begin{Bmatrix}\hat{C}_1^{n+1}\\ \hat{C}_2^{n+1}\end{Bmatrix} = \begin{bmatrix}1+e^{-\frac{\Delta E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)}\left(2k^4-\frac{2k^3Q_1}{1+\beta\left(T_0-T\right)}\right)\Delta t & -\frac{2e^{-\frac{\Delta E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)}k^3Q_2\Delta t}{1+\beta\left(T_0-T\right)}\\ -\frac{2e^{-\frac{\Delta E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)}Sk^3Q_2\Delta t}{1+\beta\left(T_0-T\right)} & 1+e^{-\frac{\Delta E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)}S\left(2Hk^4-\frac{2k^3Q_3}{1+\beta\left(T_0-T\right)}\right)\Delta t\end{bmatrix}^{-1}$$
$$\times\left[\begin{Bmatrix}\hat{C}_1^{n}\\ \hat{C}_2^{n}\end{Bmatrix} - e^{-\frac{\Delta E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)}k^2\Delta t\begin{Bmatrix}\hat{P}_1^{n}\\ S\hat{P}_2^{n}\end{Bmatrix}\right] \tag{32}$$

---

[4] $\begin{bmatrix}a & b\\ c & d\end{bmatrix}^{-1} = \frac{1}{ad-cb}\begin{bmatrix}d & -b\\ -c & a\end{bmatrix}$

The concentrations are calculated as follows (Figure 3). In real space, we use *C* to calculate *P*. Then we transform *C* and *P* to find $\widehat{C}^n$ and $\widehat{P}^n$. In Fourier space we use $\widehat{C}^n$ and $\widehat{P}^n$ to calculate $\widehat{C}^{n+1}$. We transform $\widehat{C}^{n+1}$ into real space and repeat the same process.

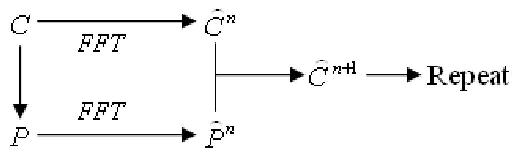

Figure 2: Procedure used to calculate the concentrations

Coordinates in Fourier Space:

The coordinates in Fourier space are not the same as those in real. Fourier space is made up of frequencies as it is also called the frequency domain/space. For a two dimensional set of data, the frequencies for each row (left to right) are

$$0, \frac{1}{N\Delta}, \frac{2}{N\Delta}, \ldots, \frac{1}{2\Delta} - \frac{1}{N\Delta}, \pm\frac{1}{2\Delta}, -\left(\frac{1}{2\Delta} - \frac{1}{N\Delta}\right), \ldots, -\frac{2}{N\Delta}, -\frac{1}{N\Delta}$$

The columns (top to bottom) follow the same sequence. The sign doesn't matter for the middle term. Δ is the sampling interval, which acts like a length scale. For example, $\Delta = 0.1$ could mean there are 0.1 nm per pixel.

Fast Fourier Transform (FFT)

If we could use Eq. 32, the calculations would be incredibly simple. Unfortunately, Eq. 32 is in Fourier space, which we can't intuitively see. In addition, we can't find a formula for the transformation of $P(x_1, x_2, t)$ because it is non-linear, that is, $\widehat{P}(k_1, k_2, t)$ can't be calculated directly in Fourier space. Also, we can't transform Eq. 32 back to real space using the Fourier transformation in the previous section because it is not in the right form.

The solution to this problem is the Fast Fourier Transformation (FFT). This is an efficient and fast algorithm for transforming data sets between real and Fourier space. The Discrete Fourier Transformation (DFT) is defined as

$$F(m_1, m_2) = \sum_{n_2=0}^{N_2-1}\sum_{n_1=0}^{N_2-1} f(n_1, n_2)\, e^{-2\pi i n_1 m_1/N_1} e^{2\pi i n_2 m_2/N_2} \tag{33}$$

F is the transformation of the discrete data set *f*. One could simply put this into a computer and obtain the transformations. However, for large data sets, say 512x512, this method can take a *very* long time. For data sets of this size, the FFT algorithm is the best solution; in fact, calculations that would take days and possibly even weeks can be reduced to merely seconds and minutes, which is an enormous advantage.

Take the one dimensional DFT $F(m) = \sum_{n=0}^{N-1} f(n)\, e^{-2\pi i n m/N}$ as an example[5]. This can be rewritten as

$$\begin{aligned} F(m) &= \sum_{n=0}^{N/2-1} f(2n)\, e^{-2\pi i m(2n)/N} + \sum_{n=0}^{N/2-1} f(2n+1)\, e^{-2\pi i m(2n+1)/N} \\ &= \sum_{n=0}^{N/2-1} f(2n)\, e^{-2\pi i m n/(N/2)} + e^{2\pi i m/N} \sum_{n=0}^{N/2-1} f(2n+1)\, e^{-2\pi i m n/(N/2)} \\ &= F^e(m) + W^m F^o(m) \end{aligned} \tag{34}$$

[5] The two dimensional DFT is a combination of two one dimension DFT's

Thus F can be written as the DFT of the even indices plus a complex constant[6] times the DFT of the odd indices. $F^e(m)$ and $F^o(m)$ are periodic with periods of length $N / 2$, thus, $F^e(m) = F^e\left(m - \frac{N}{2}\right)$ and $F^o(m) = F^o\left(m - \frac{N}{2}\right)$ for $m \geq \frac{N}{2}$. F originally requires N^2 operations, but, by separating it into evens and odds, F now only requires $\frac{N^2}{2}$ operations, which is slightly faster. We continue breaking F down into smaller sets of size $N / 4$ of evens and odds[7] and so on until we are left with sets of size 1. F eventually only requires $N \log_2 N$ operations, which is significantly faster for large N. In the end, we have a seemingly meaningless string of *e*'s and *o*'s. Actually, this seemingly meaningless string is extremely useful in finding which $f(n)$ goes with $F^{eeoeoo....oeoe}(m)$. Take the string, reverse it, and let $e = 0$ and $o = 1$. What does this produce? It produces the binary representation of n (in $f(n)$) (Press et al.2002)! Thus, a faster way to break down F until there are N sets of size 1 left is by taking the binary representation of the indices of the initial set and "flipping" them. This is called bit reversing, the first part of the FFT.

Once we have bit reversed the initial set, we have to regroup everything. This method is called the butterfly method[8], which is also known as the Danielson-Lanzos Formula. The amazing aspect of this formula is that it is iterative. The butterfly method first takes two consecutive elements (after bit reverse) and combines them into a set of size two. Each element of the new set is calculated using a similar formula as that of Eq. 34. There are $N / 2$ such sets. Then, two consecutive sets are combined to create a new set of size four (one element of one set

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[6] Note that W is not the same constant for each successive separation of F. For each successive separation after Eq. 34, the N in W is divided by two.

[7] $F^e(m) = F^{ee}(m) + W^m F^{eo}(m) \qquad W^m = e^{2\pi i m / (N/2)}$

[8] When this method is drawn out, parts of it are shaped like a butterfly.

combines with an element of the other) using a similar formula. There are *N* / 4 such sets. This continues until you are left with one large set of size *N*, which is the transformation. The following is a diagram for combining the elements (size 8). The left side is already bit reversed.

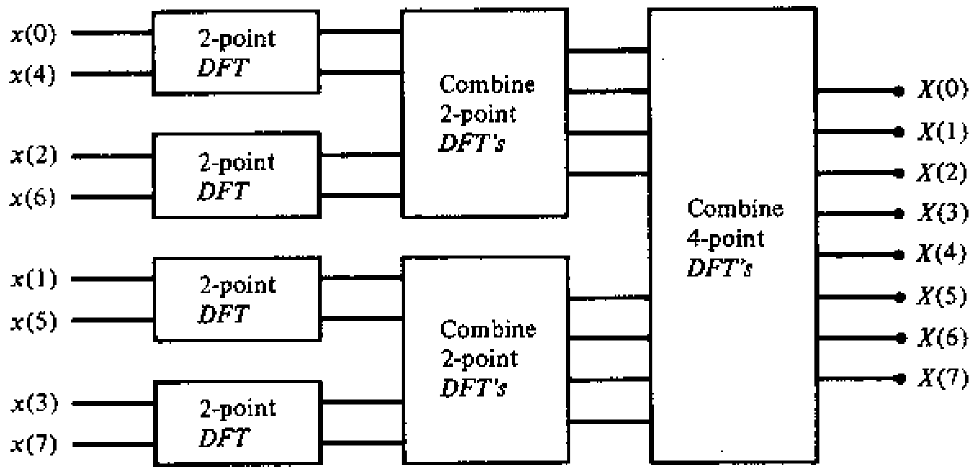
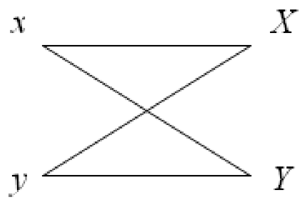


Figure 3: Method of combining elements after bit reversing.
http://www.cmlab.csie.ntu.edu.tw/cml/dsp/training/coding/transform/fft.html

The following is a simple 2 point DFT



$$
\begin{aligned}
&N = 2 \\
&F^e(1) = F^e(2) \\
&F^o(1) = F^o(2) \\
&X = F^e(1) + W^1 F^o(1) = x + \left(e^{2\pi i/2}\right)^1 y = x - y \\
&Y = F^e(2) + W^2 F^o(2) = F^e(1) + W^2 F^o(1) = x + \left(e^{2\pi i/2}\right)^2 y = x + y
\end{aligned}
\tag{35}
$$

The FFT cannot simulate an infinitive domain. To resolve this problem, the simulation is carried out in a square cell, which is replicated many times to cover the whole space (Lu and Kim, 2005).

Numerical Stability and Convergence Analysis

We have found that Eq. 32 is very sensitive to time step Δt and sampling interval Δ. We did numerical convergence test in order to choose appropriate Δt and Δ. See Appendix A for discussion.