Numerical Solution of the Kinetics of Spinodal Decomposition

Submitted to:

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<u>Motivation</u>

The formation of polymer porous membranes is usually done through either phase inversion or thermally induced phase separation (TIPS). The phase inversion process uses a nucleation and growth mechanism, where the polymer and diluent phases will separate and grow from heterogeneous nucleation sites. Because all nucleation does not occur at one time step, a wide pore size distribution is usually a result of this mechanism. The TIPS process uses the mechanism of spinodal decomposition to separate the polymer and diluent phases. This mechanism is a spontaneous phase separation, leading to a reticulate structure of polymer-rich matrix surrounding diluent-rich domains. The distribution of pore sizes is typically much narrower for this method than it is for nucleation and growth. Diffusion, in this case, proceeds up concentration gradients, anomalous to typical diffusion. Understanding the kinetics of spinodal decomposition and developing a preliminary model will help in the preparation of membranes by TIPS.

Parallel to Surface Phenomena

This project does not directly apply the concepts developed in class, but the form of the equation to be analyzed is the same form as the equation of spinodal de-wetting of thin films. The de-wetting equation describes the stability of a thin film when both curvature and Van der Waals forces are considered. In addition, one of the initial principles introduced in class was the idea of the "Gibbs dividing surface," describing a region between two phases. Most of the techniques developed in class have assumed this surface to be infinitesimally small. The system investigated here will develop how the concentration will change between the two separating phases, similar to a Gibbs dividing surface.

Problem Description and Theory Development

The kinetics of spinodal decomposition can be described by Equation (1), proposed by J. Cahn:

$$\frac{\partial c}{\partial t} = M * \left[\left(\frac{\partial^2 f}{\partial c^2} \right) \nabla^2 c - 2 K \nabla^4 c \right]$$
(1)

In this equation, c is the polymer concentration, M is the diffusion mobility, f is the free energy of a unit volume of molecules of homogeneous material of composition c, and K is the gradient energy coefficient. In order to solve this problem, we must first non-

dimensionalize the equation. We will define the following initial conditions and nondimensional parameters:

Initial Condition:
$$C = C_{0}$$

Nondimensional parameters:
 $\overline{C} = \frac{C}{C_{0}}$ (dimensionless concentration)
 $\tau = \frac{t}{t_{c}}$ (dimensionless time)
 $\overline{\nabla}^{2} = \frac{1}{L_{c}^{2}}\overline{\nabla}^{2}$ (dimensionless gradient operator)

In these relationships, c_o is the initial concentration of the homogeneous sheet, t_c is a characteristic time, and L_c is a characteristic length. Both the characteristic time and length will be parameters specific for the polymer/diluent system being investigated. Using these transformations, the Cahn-Hilliard equation can be re-written in the form:

$$\frac{\partial \overline{c}}{\partial \tau} = \alpha G(\overline{c}) \overline{\nabla}^2 \overline{c} - \beta \overline{\nabla}^4 \overline{c}$$

$$\alpha = \frac{M}{L_c^2}$$

$$\beta = \frac{2K}{L_c^4} \overline{L_c^4}$$

$$G(\overline{c}) = \left(\frac{\partial^2 f}{\partial \overline{c}^2}\right) = (1 + \delta(c^2 - c))$$
(2)

The coefficients α and β are dimensionless terms that will be set to unity for this investigation. G(c) is assumed to have parabolic form, concave up with a dimensionless parameter δ describing the shape of the parabola. A plot of G(c) with varying δ can be found in the Appendix.

Numerical Solution Technique

The partial differential equation to be solved is nonlinear, due to the concentration dependence of the G coefficient in the first term. This nonlinearity makes it difficult to solve the differential equation analytically, so numerical analysis will be used. The technique, developed in the Appendix, is a fully implicit, one-dimensional approach using finite difference to discretize the position and time steps. The nonlinearity is removed by time lagging the G(c) coefficient, or evaluating it at the current time step. The resulting system of linear equations is solved using an LU decomposition algorithm, and then returned for the next time step. Because both the time and position directions are dimensionless variables, the step size in both will be set to unity. Additionally, a two-

dimensional plane has been derived, using an equally spaced grid for the dimensionless x- and y-directions.

Assumptions

For this evaluation, all other contributing forces that would affect the energy of the system have been neglected. Spinodal decomposition is known to be a very rapid spontaneous event when the circumstances for instability are present, so this assumption seems valid. A general form of the second derivative of free energy with concentration has also been assumed as a parabola, concave up. The free energy relationship with concentration is specific for each polymer/diluent evaluated, however, and unusual phase diagrams can lead to non-parabolic free energy relationships. These cases have been ignored, but can be accounted for with more specific free energy information. Finally, boundary effects have been ignored. This assumption is implemented through the use of periodic boundary conditions for the ends of both the one- and two-dimensional domains.

Results and Discussion

The following parameters were investigated in this project:

- 1) Base Case Uniform initial concentration, with an impulse increase in one entry creating the initial concentration gradient.
- 2) Effect of location of the initial impulse.
- 3) Effect of magnitude of the initial impulse.
- 4) Effect of magnitude of the G coefficient.
- 5) Effect of initial homogeneous concentration.
- 6) Effect of an initial concentration gradient (no initial impulse was necessary for this case).
- 7) Two-dimensional base case with de-stabilizing G value.

The base case will be taken as initial concentration of 0.5, curvature value δ of the G coefficient equal to 6, and impulse concentration equal to 2 at grid position 20. As can be seen in Figure 1, the base case shows a spontaneous separation into alternating domains having high and low concentrations, in a sinusoidal response with a determinable amplitude and wavelength.

As is predicted by spinodal decomposition theory, the system should become stable in regions where G is positive so the domains will continue to spinodally decompose until G has increased enough to approach positive numbers. For the base case, G equals zero at approximately 0.22 and 0.78, and the peaks and valleys of the concentration profile approaches numbers near to these limits. Natural diffusion occurring down concentration gradients will also limit the final steady state value. The base case approaches 0.26 and 0.74 for peaks and valleys, so this result appears consistent.



Figure 1: Base case result, with injected impulse at site 20

The effect of position of the initial impulse showed no effect on the kinetics of the phase separation, as expected due to the periodic boundary conditions leading to only a phase shift in the concentration profile. The initial magnitude of the impulse also showed minimal impact on the shape of the decomposed concentration profile. The plots from the magnitude and location of initial impulse will not be included here, due to brevity considerations.

The effect of the G coefficient is predictable in that it should change the concentration limits that the domains will approach, and will even stabilize the system if the initial concentration is exposed to a positive G coefficient. The result, however, shows a significant time effect as well. As the negative degree of G is reduced, longer time is necessary for steady state to be reached (Figure 2), and inversely, a more negative G leads to a more rapid concentration decomposition (Figure 3). Figure 4 shows the effect of an impulse change in a positive G environment, and the stabilizing absorption of the impulse.

When an initial homogeneous concentration in the positive range of G was selected, stabilization similar to the positive G result shown in Figure 4 was obtained, as expected. The profile of this result is not included here. When the initial concentration was set above the critical concentration to maintain negative G but below the base case value, another interesting result was observed, as can be seen in Figure 5. This problem then becomes non-symmetrical, allowing less material to diffuse from the valleys to raise the peaks to their steady state values. After the number of time cycles for the base case, the peaks off phase from the initial impulse have still not reached steady state. In addition, the peak and valley values are slightly higher than the base case and the wavelength of the sinusoidal response is longer.



Figure 2: Parabolic Factor δ decreased to 5.



Figure 3: Parabolic Factor δ increased to 8.



Figure 4: Parabolic Factor δ decreased to 2 (Stabilizing condition).



Figure 5: Initial homogeneous concentration decreased to 0.3.

The last one-dimensional case, illustrated in Figure 6, investigates the effect of a linear initial concentration gradient instead of an impulse disturbance. The sinusoidal response still develops, with a comparable wavelength and amplitude at steady state. The path to get to steady state, however, is quite different from the base case decomposition. The sinusoidal response begins along the gradient and slowly expands with time cycles away from the initial gradient, ultimately becoming independent at steady state.



Figure 6: Initial concentration gradient replacing initial impulse disturbance.

Finally, a single two-dimensional case has been evaluated, investigating the base case from the one-dimensional model. The result from this case is very unusual, as it suggests a different steady state result from the 1-D case. In the initial time cycles, circular domains develop, suggesting something similar to a two-dimensional sinusoidal response. As time progresses, however, these domains break up into an infinite sinusoidal sheet, traveling along the diagonal of the domain. This result suggests further investigation is necessary to understand the differences between one-dimensional and two-dimensional behaviors. Three dimensional and contour representations for the two-dimensional model can be seen in Appendix B.

Conclusion

Through the numerical analysis of the partial differential equation proposed by Cahn, a rudimentary kinetic model has been developed to describe the mechanism of spinodal decomposition. This model shows the dependence of spinodal decomposition on the thermodynamics of the polymer/diluent system and the location, magnitude, and type of disturbance applied to initiate phase separation. A similar method has proposed a very basic two-dimensional representation of spinodal decomposition, but the predicted result is significantly different from the one-dimensional case, opening new areas for future investigation.

The data from the models is dimensionless and needs physical mobility and thermodynamic data to determine characteristic lengths and times for the spinodally decomposing domains. For this reason, only general trending was done in this analysis, ignoring some of the subtleties like small changes in the wavelengths or amplitudes of the sinusoidal responses.

<u>Reference</u>

Cahn, J.W. "Spinodal Decomposition." *Transactions of the Metallurgical Society of AIME*. 242, pp. 160-180 (February 1968).