# Phase Separation in Binary Mixture via Conservative Volume Force

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## Abstract

We present a mathematical model that describes the spinodal decomposition of a binary (oil-water) mixture excited by a conservative volume force, here taken to be the potential of a surface acoustic wave (SAW) propagating in the underlying substrate.

Taking an energetic approach to modeling this problem, energy equations are introduced for both components in the mixture which account for all hydrodynamic effects considered. Further, constitutive laws for the component fluxes and velocities, that are consistent with the second law of thermodynamics, are derived by requiring the free-energy functional of the binary mixture to be decreasing in time [1]. Finally, conservation of mass requires the concentration of each component be a conserved quantity. Combining all of these equations yields a system of two PDEs for the concentration of one component and the underlying pressure profile that can be solved numerically.

## Motivation

Binary mixtures are omnipresent from fabricated metal alloys to modeling tumor growth. Creating a theoretical framework derived from first principles is essential to understanding how they evolve. In oil-water mixtures, phase separation problems arise as a result of increasing interest in water recovery. Experimental results shown in Figure 1 provide a proof-of-concept for obtaining separation via a SAW propagating in the underlying substrate. Both experiments show a thin-film of pure-oil being dragged out of the emulsion leaving behind pure water.

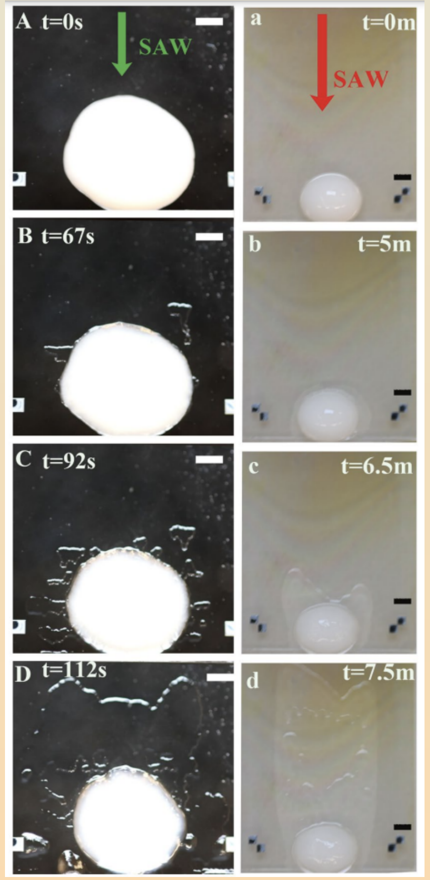
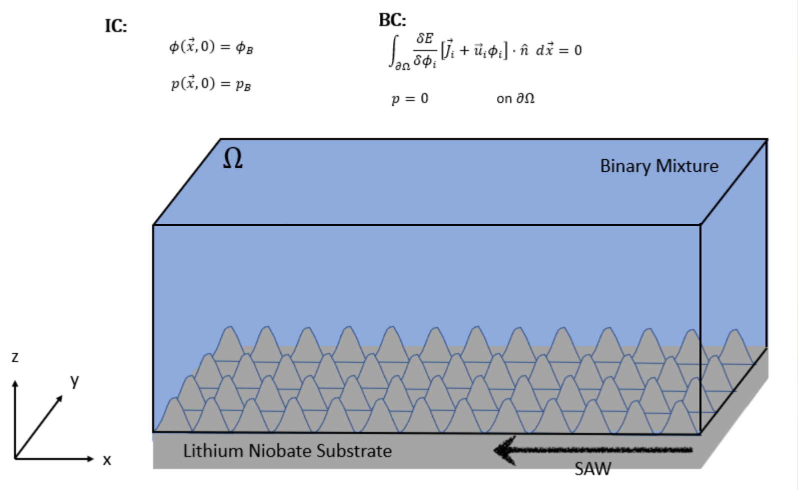


*Fig. 1: An oil*-water emulsion atop lithium niobate substrate initially at rest. As SAWs propagate through the underlying substrate, a thin film of oil is dragged out in opposition to the propagating SAW. Left behind is a nearly pure drop of water. Results on the left are simulated using a high-humidity environment while those on the right are in a low-humidity environment. As evident, a high-humidity environment slows phase separation.

## Main assumptions

- Mixture satisfies no-voids constraint
$$\phi_o + \phi_w = 1$$
- Mixture satisfies concentration of mass
$$\vec{J}_o + \vec{J}_w = 0$$
- Component densities are constant and equal
- Diffusive flux of components occurs solely from concentration gradients in solution
- SAW force exponentially decays in fluid as it attenuates [2]
- Cahn-Hilliard type formulation of free-energy functional with Flory-Huggins form of free-energy per unit volume is applicable [3]
- Symmetric binary fluid: oil-oil and water-water interactions are modeled identically
- Neglect free-surface dynamics and consider phase separation in a confined box



**IC:**

$$\phi(\vec{x},0) = \phi_B$$

$$p(\vec{x},0) = p_B$$

**BC:**

$$\int_{\partial\Omega} \frac{\delta E}{\delta \phi_i}\left[\vec{J}_i + \vec{u}_i\phi_i\right]\cdot \hat{n}\ d\vec{x} = 0$$

$$p = 0 \qquad \text{on } \partial\Omega$$

*Fig. 2:* Sketch of the problem being modeled in 3D with conservative volume force from SAW

## Equations

Evolution equation and conservation of mass for the mixture: $(\phi = \phi_o, \quad \phi_w = 1-\phi)$

$$\frac{\partial \phi}{\partial t} + \nabla\cdot(\vec{u}_o\phi + \vec{J}\,) = 0$$

$$\nabla\cdot\left(\phi\vec{u}_o + (1-\phi)\vec{u}_w\right) = 0$$

Thermodynamically consistent component velocity and flux expressions [1]:

$$\vec{u}_o = -(k+k_o)\left[\nabla p + \rho\nabla\psi - 2\frac{\delta E}{\delta\phi}\nabla\phi\right] - 2k_o(1-\phi)\nabla\frac{\delta E}{\delta\phi}$$

$$\vec{u}_w = -(k+k_w)\left[\nabla p + \rho\nabla\psi - 2\frac{\delta E}{\delta\phi}\nabla\phi\right] + 2k_w\phi\nabla\frac{\delta E}{\delta\phi}$$

$$\vec{J} = -M\phi\nabla\frac{\delta E}{\delta\phi}$$

Associated energy of mixture:

$$E[\phi] = \int_\Omega f(\phi) + \frac{\epsilon^2}{2}|\nabla\phi|^2 + \rho\psi(\vec{x}\,)\ d\vec{x}$$

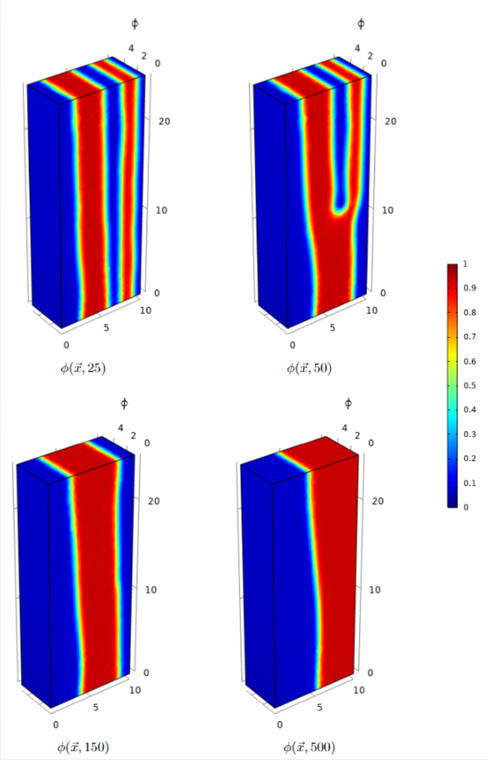
$\psi$ : Conservative Volume Force

| $k$ | $k_o$ | $k_w$ | $\rho$ | $M$ | $\epsilon^2$ | $\lambda$ | $\alpha$ | $A$ | $\omega$ |
|---|---|---|---|---|---|---|---|---|---|
| .00015 | .0001 | .0002 | 997 | .0002 | 4.8613 | 2.47 | 1370 | $10^{-10}$ | $5\cdot10^7$ |
| $\frac{L^3T}{M}$ | $\frac{L^3T}{M}$ | $\frac{L^3T}{M}$ | $\frac{M}{L^3}$ | $\frac{L^3T}{M}$ | $\frac{ML}{T^2}$ | 1 | $\frac{1}{L}$ | $L$ | $\frac{1}{T}$ |
| Mass Averaged Mobility | Mobility of Oil | Mobility of Water | Matched Density | Diffusion Coefficient | Interfacial Energy Coefficient | Ratio of Attenuation Lengths of SAW in $x$ and $z$ | Inverse Attenuation Length of SAW in $x$ | Max Displacement of Solid Substrate from SAW | Frequency of SAW |

*Fig. 3:* Parameters in the model where the rows give: the symbol, the numerical value used in simulations, the respective dimension, and a physical description

## Results

*Fig. 4:* Evolution of concentration profile, $\phi$, with conservative volume force, $\psi = (1+\lambda^2)A^2\omega^2 e^{-\alpha(x+\lambda z)}$, from propagating SAW [2]



Model leads to solutions that decompose into its constituent components.

Evolution is initially dominated by vertical stratification into ultra-high and ultra-low concentration domains.

At long times, the domains slowly coarsen until solution consists of two pure phases separated by a single diffuse interface

## Future Work

- Introduce free-surface dynamics via kinematic boundary condition and assumption of small aspect ratio [4]
- Consider mixtures of unequal densities

## References

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[4] Naraigh, L., Thiffeault, J. Nonlinearity. (2010).