Nonlinear dynamics of phase separation in thin films

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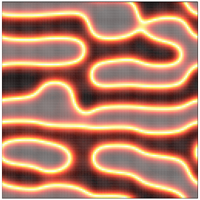
Phase separation in thin layers

- Many practical reasons for studying phase separation in thin layers.
- Thin polymer films are used in the fabrication of semiconductor devices.
- Paints and coatings, which are typically mixtures of polymers.
- Self-assembly: molecules respond to an energy-minimisation requirement by spontaneously forming large-scale structures.
- Main reason: it's a nice problem.

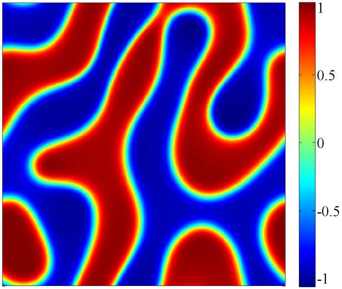


Cahn–Hilliard Equation

The celebrated Cahn–Hilliard equation:

$$\frac{\partial c}{\partial t} = D\nabla^2\left(c^3 - c - \gamma\nabla^2 c\right)$$

- $c = \pm 1$ indicates total segregation (phase separation)
- Natural evolution is to phase separate into domains or bubbles
- D a diffusion coefficient
- $\sqrt{\gamma}$ gives the typical width of interface



NSCH Equations

The Navier–Stokes Cahn–Hilliard equations:

$$\frac{\partial \mathbf{v}}{\partial t} + \mathbf{v}\cdot\nabla\mathbf{v} = \nabla\cdot T - \frac{1}{\rho}\nabla\phi, \qquad \nabla\cdot\mathbf{v} = 0,$$

$$\frac{\partial c}{\partial t} + \mathbf{v}\cdot\nabla c = D\nabla^2\left(c^3 - c - \gamma\nabla^2 c\right)$$

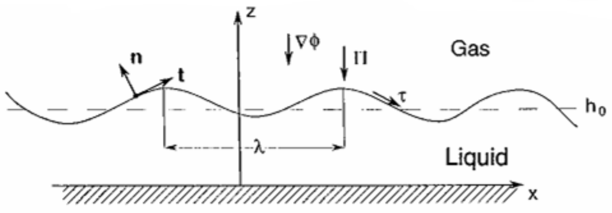
$$T_{ij} = -\frac{p}{\rho}\delta_{ij} + \nu\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right) - \beta\gamma\frac{\partial c}{\partial x_i}\frac{\partial c}{\partial x_j}$$

- The concentration c is dragged by the fluid, but also dynamically feeds back on the fluid motion by exerting a stress, due to its tendency to phase separate.
- ϕ is a body-force potential
- This is of course a tough set of equations to solve...
- See for instance Ding et al. (2007).

Long-wavelength expansion

To get a simple model that includes the dynamical feedback, make a long-wave expansion for a thin film with a free surface.

Assume he scale of lateral variations ℓ is large compared with the scale of vertical variations h_0. The parameter $\delta = h_0/\ell$ is small.



Thin-film NSCH equations

$$\frac{\partial h}{\partial t} + \frac{\partial J}{\partial x} = 0$$

$$\frac{\partial}{\partial t}(ch) + \frac{\partial}{\partial x}(Jc) = \frac{\partial}{\partial x}\left(h\frac{\partial \mu}{\partial x}\right)$$

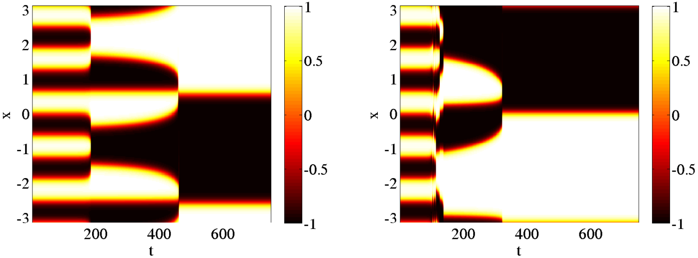
$$J := -\tfrac{1}{3}h^3\left\{\frac{\partial}{\partial x}\left(-\frac{1}{C}\frac{\partial^2 h}{\partial x^2} + \phi\right) + \frac{r}{h}\frac{\partial}{\partial x}\left[h\left(\frac{\partial c}{\partial x}\right)^2\right]\right\}$$

$$\mu := c^3 - c - C_{\mathrm{n}}^2\frac{1}{h}\frac{\partial}{\partial x}\left(h\frac{\partial c}{\partial x}\right)$$

$$r := \frac{\delta^2\beta\gamma}{D\nu}, \qquad C_{\mathrm{n}} := \frac{\delta\sqrt{\gamma}}{h_0}, \qquad C := \frac{\nu\rho D}{h_0\sigma\delta^2}$$

Numerical solution

Typical run: an initial $c(x,0)$ with several domains coarsens into two large domains:



Coalescence is faster with a larger backreaction constant r (right).

$\Longrightarrow$ h drives c into an equililbrium.

Proposition (Existence of a decreasing functional)

Given a smooth solution (h, c) to the thin-film NSCH equations, positive in the sense that $h(x,t) > 0$, and a continuous potential function ϕ, then the functional

$$\mathcal{F}[h,c] = \int_0^L dx \left[\frac{1}{2C}\left(\frac{\partial h}{\partial x}\right)^2 + \int^h \phi(s)\, ds\right] + \frac{r}{C_{\mathrm{n}}^2}\int_0^L dx\, h\left[\tfrac{1}{4}\left(c^2-1\right)^2 + \frac{C_{\mathrm{n}}^2}{2}\left(\frac{\partial c}{\partial x}\right)^2\right]$$

is non-increasing, $\dot{\mathcal{F}} \le 0$.

$\Longrightarrow$ Existence of a positive Lyapunov functional.

Proposition (Hölder continuity of $h(x, \cdot)$)

If (h, c) is a smooth, positive solution to the thin-film NSCH equations, in the sense that $h(x, t) > 0$, and if the potential function ϕ has a positive anti-derivative, then $h(x, \cdot)$ is Hölder continuous, with time-independent Hölder constant k_H.

Proposition (An upper bound on the height field)

If (h, c) is a smooth, positive solution, in the sense that $h(x, t) > 0$, and if the potential function ϕ has a positive anti-derivative, then $h(x, \cdot)$ is bounded above.

Full regularity

Specific choice for the potential (repulsive Van der Waals):

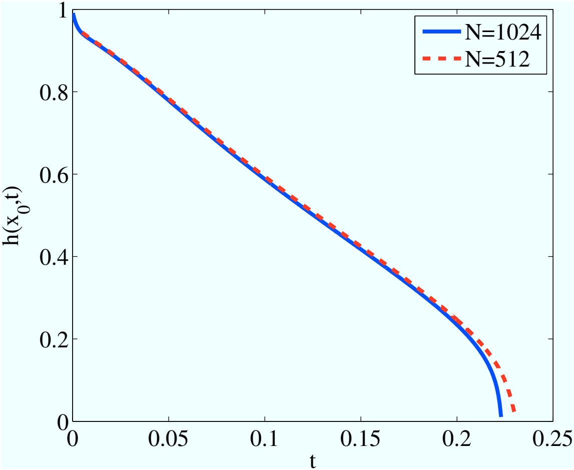
$$\phi = -\frac{G}{2s^3}\,, \qquad G > 0.$$

Proposition (No-rupture condition for the potential)

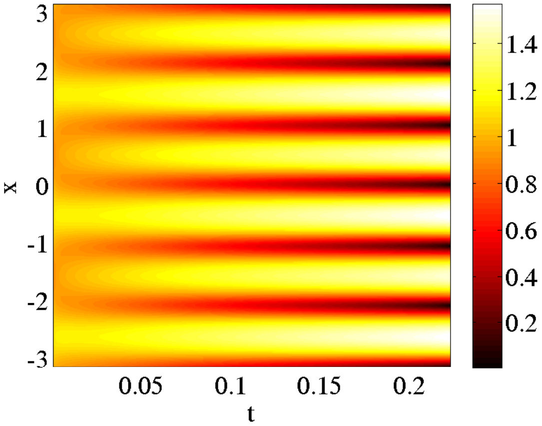
If (h, c) is a smooth, positive solution to the thin-film NSCH equations equations, in the sense that $h(x,t) > 0$, and if the potential function ϕ has the form above then there is an a priori, time-independent lower bound on h.

Film rupture

In the absence of a regularizing potential, can apparently get film rupture in finite time.



Rupture (cont'd)



Conclusions

- Long-wave expansion for Navier–Stokes Cahn Hilliard equations;
- Can prove some regularity properties;
- Regularizing potential can be proved to prevent rupture;
- Without a potential, rupture may happen. Does it?
- Mechanism for rupture is not clear;
- Any experimental evidence for this rupturing tendency? Need guidance.

Aarts, D. G. A. L., Dullens, R. P. A. & Lekkerherker, H. N. W. 2005 Interfacial dynamics in demixing systems with ultralow interfacial tension. *New J. Phys.* **7**, 14.

Bray, A. J. 1994 Theory of phase-ordering kinetics. *Adv. Phys.* **43**, 357–459.

Cahn, J. W. & Hilliard, J. E. 1957 Free energy of a nonuniform system. I. Interfacial energy. *J. Chem. Phys* **28**, 258–267.

Cohen, D. S. & Murray, J. D. 1981 A Generalized Diffusion Model for Growth and Dispersal in a Population. *J. Math. Biology* **12**, 237.

Ding, H., Spelt, P. D. M. & Shu, C. 2007 Diffuse interface model for incompressible two-phase flows with large density ratios. *J. Comp. Phys.* **226**, 2078.

Elder, K. R., Rogers, T. M. & Desai, R. C. 1988 Early stages of spinodal decomposition for the Cahn–Hilliard–Cook model of phase separation. *Phys. Rev. B* **38**, 4725.

Karim, A., Douglas, J. F., Sung, L. P. & Ermi, B. D. 2002 Self-assembly by phase separation in polymer thin films. *Encyclopedia of Materials: Science and Technology* p. 8319.

Kim, D. & Lu, W. 2006 Interface instability and nanostructure patterning. *Comp. Mater. Sci.* **38**, 418–425.

Krausch, G., Kramer, E. J., Rafailovich, M. H. & Sokolov, J. 1994 Self-assembly of a homopolymer mixture via phase separation. *Appl. Phys. Lett.* **64**, 2655.

Lowengrub, J. & Truskinowsky, L. 1998 Quasi-incompressible Cahn–Hilliard fluids and topological transitions. *Proc. R. Soc. Lond. A* **454**, 2617–2654.

Lu, W. & Salac, D. 2005 Patterning Multilayers of Molecules via Self-Organization. *Phys. Rev. Lett.* **94**, 146103.

Mertens, K., Putkaradze, V., Xia, D. & Brueck, S. R. 2005 Theory and experiment for one-dimensional directed self-assembly of nanoparticles. *J. App. Phys.* **98**, 034309.

Ó Náraigh, L. & Thiffeault, J.-L. 2007a Bubbles and Filaments: Stirring a Cahn–Hilliard Fluid. *Phys. Rev. E* **75**, 016216.

Ó Náraigh, L. & Thiffeault, J.-L. 2007b Dynamical effects and phase separation in cooled binary fluid films. *Phys. Rev. E* **76**, 035303(R).

Ó Náraigh, L. & Thiffeault, J.-L. 2007b Nonlinear dynamics of phase separation in thin films. `http://arxiv.org/abs/0911.0583`.

Xia, D. & Brueck, S. 2004 A facile approach to directed assembly of patterns of nanoparticles using interference lithography and spin coating. *Nano Letters* **4**, 1295.

Zhu, J., Shen, L. Q., Shen, J., Tikare, V. & Onuki, A. 1999 Coarsening kinetics from a variable mobility Cahn–Hilliard equation: Application of a semi-implicit Fourier spectral method. *Phys. Rev. E* **60**, 3564–3572.