Contents

1 Cahn–Hilliard Surface Tension Calculation

Note: The Cahn-Hilliard calculation was done for the case of conserved-order parameter i.e. the total order parameter volume $\int c dx = \bar{c}$ is conserved. For a 2 phase system, $\bar{c} = \phi_a c_a + \phi_b c_b$ where $\phi_a + \phi_b = 1$. The phase separation process starts with a fixed $\bar{c}$ and it is then perturbed. The system selects fractions ϕ_a, ϕ_b dynamically in order to lower the free energy.

This note outlines the surface tension calculation in a Landau-Ginzburg framework, as applied in our body force paper. The system consists of a binary fluid mixture with two stable compositions, c_α and c_β, where c denotes the mole fraction of species B in an A-B mixture. The free energy density has local minima at these two concentrations.

Expanding the free energy leads to a functional of the form:

$$f(c) = f_0(c) + \Gamma_1 (\nabla c)^2 + \Gamma_2 \nabla^2 c + \dots \tag{1}$$

We consider a 1D interfacial profile where $c(x) \to c_\alpha$ as $x \to -\infty$ and $c(x) \to c_\beta$ as $x \to \infty$. The aim is to compute the excess free energy due to the interface—i.e., the surface tension σ.

1.1 First Integral via Variational Principle

To minimize the functional

$$\int_{-\infty}^{\infty} F(\phi, \partial_x \phi)\, dx,$$

the Euler–Lagrange equation gives:

$$\frac{\partial F}{\partial \phi} = \partial_x \left(\frac{\partial F}{\partial \partial_x \phi} \right). \tag{2}$$

If F has no explicit x-dependence, we obtain:

$$\frac{\partial F}{\partial x} = \frac{\partial F}{\partial \phi} \partial_x \phi + \frac{\partial F}{\partial (\partial_x \phi)} \frac{\partial^2 \phi}{\partial x^2} \tag{3}$$

which from previous equation becomes:

$$\frac{\partial F}{\partial x} = \partial_x \frac{\partial F}{\partial (\partial_x \phi)} \partial_x \phi + \frac{\partial F}{\partial (\partial_x \phi)} \frac{\partial^2 \phi}{\partial x^2} = \partial_x \left(\frac{\partial F}{\partial (\partial_x \phi)} \partial_x \phi \right) \tag{4}$$

which implies the conserved quantity:

$$F - \partial_x \phi \cdot \frac{\partial F}{\partial \partial_x \phi} = \text{const.} \tag{5}$$

This is analogous to energy conservation when the Lagrangian lacks explicit time dependence.

1.2 Interface Free Energy

Assume a 1D system with phase α for $x < 0$ and phase β for $x > 0$. Let $f(c)$ be the bulk free energy density and $c(x)$ the concentration profile interpolating between c_α and c_β.

At equilibrium, the chemical potential $\mu = \frac{\partial f}{\partial c}$ must be constant throughout, i.e.,

$$\partial_x \mu = \partial_x \left(\frac{\partial f}{\partial c} \right) = 0.$$

In a mixed phase of volume fraction ϕ of phase α, the total concentration is:

$$c = \phi c_\alpha + (1 - \phi) c_\beta,$$

and assuming additivity (no entropy of mixing), the free energy is:

$$f_{\text{mix}} = \phi f(c_\alpha) + (1 - \phi) f(c_\beta),$$

which corresponds to the common tangent construction between c_α and c_β.

Common Tangent Construction and Phase Separation

In systems with a conserved order parameter (e.g., concentration), phase separation is governed by the geometry of the free energy density $f(c)$. When $f(c)$ is non-convex (e.g., a tilted double-well), the system can lower its total free energy by separating into two coexisting phases.

Key Principles

- The concentrations c_α and c_β of the two coexisting phases are found by the **common tangent construction**.
- These points **do not generally correspond to the minima** of $f(c)$; rather, they satisfy:

  $$\left. \frac{df}{dc} \right|_{c_\alpha} = \left. \frac{df}{dc} \right|_{c_\beta} = \mu,$$

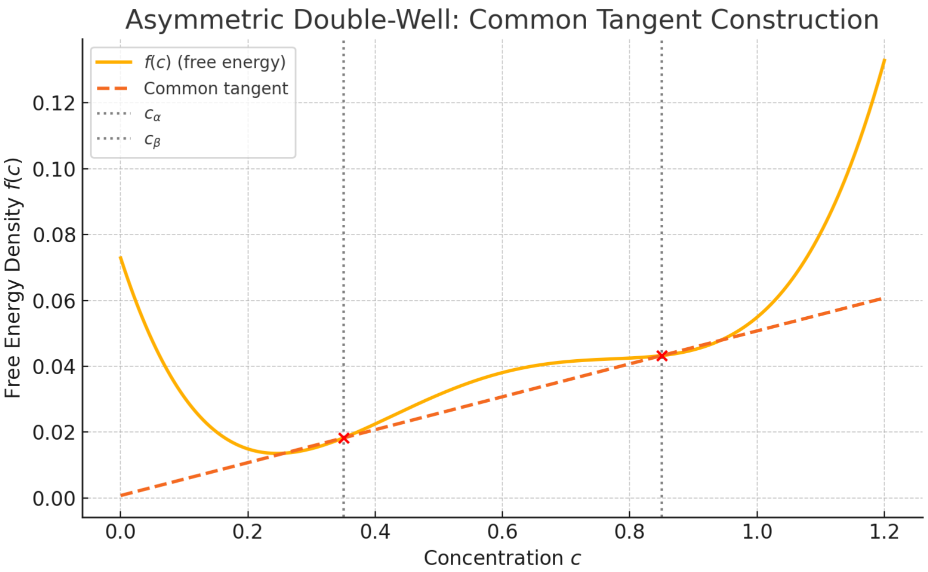
  where μ is the common **chemical potential**.
- The system develops distinct spatial domains of c_α and c_β, separated by narrow interfacial regions.
- The total free energy per unit volume is given by:

  $$f_{\text{eff}}(\bar{c}) = \phi_\alpha f(c_\alpha) + \phi_\beta f(c_\beta),$$

  where $\bar{c} = \phi_\alpha c_\alpha + \phi_\beta c_\beta$ and $\phi_{\alpha,\beta}$ are the volume fractions.
- Graphically, f_{eff} lies on the common tangent line connecting $f(c_\alpha)$ and $f(c_\beta)$, lying below the original $f(c)$ curve.

Visual Interpretation

The common tangent defines the lowest convex combination of free energy densities the system can achieve, consistent with conservation. In asymmetric potentials, the coexisting phases are shifted away from the local minima and are determined solely by the common tangent criteria.



- The minima are at $c = 0.2$ and $c = 0.8$, while the common tangent touches $c = 0.25, 0.75$ respectively.
- When they form spatial regions of distinct phases, a blob of certain phase doesn't have the exact concentration it would if it was at a minima of the potential. It instead has a different concentration (larger or smaller) than the local minima where the derivative $df/dc = \mu$.

Determining the Chemical Potential in Phase Separation

Setup

We consider a free energy density function $f(c)$, with a conserved order parameter $c \in [0, 1]$, and a fixed average concentration $\bar{c}$. The system phase-separates into two coexisting phases with concentrations c_α and c_β.

Equilibrium Conditions

The system chooses c_α, c_β, and a chemical potential μ, such that:

1. **Common chemical potential:**

$$\frac{df}{dc}(c_\alpha) = \frac{df}{dc}(c_\beta) = \mu$$

2. **Common tangent condition (equal pressure):**

$$\mu = \frac{f(c_\beta) - f(c_\alpha)}{c_\beta - c_\alpha}$$

3. **Lever rule (conservation constraint):**

$$\bar{c} = \phi_\alpha c_\alpha + \phi_\beta c_\beta, \quad \phi_\alpha + \phi_\beta = 1$$

4. **Free energy minimization:**

$$f_{\text{total}} = \phi_\alpha f(c_\alpha) + \phi_\beta f(c_\beta) \quad \text{is minimized}$$

Interpretation

- The chemical potential μ is not imposed externally, but determined implicitly by the average concentration $\bar{c}$.
- For each μ, you can find the associated pair (c_α, c_β) satisfying the common tangent condition.
- Among all such pairs, only the one that satisfies the lever rule for your given $\bar{c}$ is physically realized.
- Therefore, μ is **selected** such that the resulting phase volumes satisfy the global conservation constraint.

1.3 Definition of Surface Tension

We define the surface tension σ as the excess free energy per unit area:

$$\begin{aligned} \sigma &= \int_{-\infty}^{\infty} [f(c(x)) - \mu_A c - \mu_B(1-c)]\, dx \\ &= \int_{-\infty}^{\infty} \left[f_0(c) + \kappa(\partial_x c)^2 - \mu_A c - \mu_B(1-c)\right] dx. \end{aligned} \tag{6}$$

Letting $\Delta f(c) = f_0(c) - \mu_A c - \mu_B(1-c)$, and minimizing σ, the Euler–Lagrange equation gives:

$$\Delta f(c) - \kappa(\partial_x c)^2 = \text{const.} \tag{7}$$

At $x \to \pm\infty$, $\partial_x c = 0$ and $f(c)$ lies on the common tangent line, so the constant is zero. Hence:

$$\partial_x c = \sqrt{\frac{\Delta f(c)}{\kappa}}. \tag{8}$$

Substituting into the expression for σ:

$$\sigma = 2\int_{-\infty}^{\infty} \Delta f(c(x)) dx = 2\int_{c_\alpha}^{c_\beta} \sqrt{\kappa \Delta f(c)}\, dc. \tag{9}$$

This is the standard result. For a quartic Landau potential, this leads to the scaling:

$$\sigma \sim (T - T_c)^{3/2},$$

near the critical temperature. The key step is defining σ as the free energy difference from the common tangent baseline.

- Since our argument is principally energy minimization of the extra energy cost over the homogenous profile of a half-laminar and half-turbulence, we can trust that the Cahn-Hilliard calculation, valid for a non-active/non-reactive system with conserved order parameter can be adapted for our problem.

1.4 Interfacial tension for active systems

See Mike Cates's notes.

- The usual definition is to consider energy difference from homogenous state a la Gibbs (1878).
- There are other definitions as well:-
  - pressure across curved surface (Laplace)
  - Capillary wave dispersion (kelvin)
  - thermal capilliary wave amplitudes etc
  -

- These definitons match for equilibrium case but not for the non-equilibrium case.
- Active systems:-
  - For Allen-Cahn (or Model A) dynamics
    where Δ_{active} cannot be derivable from a free energy. An example term is $\lambda(\nabla\phi)^2$.

$$\partial_t \phi = -\frac{\partial F}{\partial \phi} + \Delta_{active} \tag{10}$$

  - For model B dynamics

$$\partial_t \phi = \nabla^2 \left(\frac{\partial F}{\partial \phi} \right) + \Delta_{active} \tag{11}$$