MODELLING: Phase Modelling & Spinodal Decomposition

We consider mathematical descriptions of how phases change with time when they are out of equilibrium.
The phase field method can allow us to model the growth of microstructures during casting etc...

Key Thermodynamics

- Gibbs free energy: $G = U - ST + PV$
- $dG = -SdT + VdP$
- ∴ At equilibrium (const P and T), G is minimised at equilibrium
- The stable phase is the one with lowest G
- Binary systems can have seperation into two phases to lower G

If a system is out of equilibrium it will change in a way to minimise its free energy:

$$\frac{d\Delta G_F}{dt} < 0$$

Functionals

A functional takes a function and turns it into a single number
A function takes a number and gives another number

The free energy depends on the phase at every point: $G = \int g(\phi(\underline{r}))d\underline{r}$

function — phase as a function of position — free energy per unit vol

To differentiate we approximate the integral to a sum:

$$\approx \sum_i g(\phi(\underline{r}_i))\delta V$$

$$= \sum_i g(\phi_i)\delta V$$

We differentiate (derivative of G must include contributions from every point)

$$dG = \sum_i \frac{\partial G}{\partial \phi_i} d\phi_i$$

$$= \sum_i g'(\phi_i) d\phi_i \delta V$$

in the limit $V \to 0$

$$\Rightarrow \int g'(\phi(\underline{r}))d\phi(\underline{r})d\underline{r}$$

Generally

For the functional $G[\phi]$:

$$dG = \int \frac{\delta G}{\delta\phi(\underline{r})} d\phi(\underline{r})d\underline{r}$$

Where in the free energy case: $\frac{\delta G}{\delta \phi(\underline{r})} = g'(\phi(\underline{r}))$

We call a function depending on infinitely many variables a functional denoted by square brackets

For differentiation: If $f[x] = \int h(x(u))du$

then $\frac{\delta f}{\delta x} = \frac{dh}{dx}$

We introduce an anzats to solve [7].

$$\frac{\partial \phi(\underline{r})}{\partial t} = -M_\phi \frac{\delta \Delta G_F}{\delta \phi(\underline{r})} \quad [8] \qquad // \; M_\phi \text{ is a +ve const.}$$

The rate of change is proportional to the energy reduction that follows a change of phase.

Substituting [8] into [7] gives: $$\frac{d\Delta G_F[\phi]}{dt} = -M_\phi \int \left(\frac{\delta \Delta G_F}{\delta \phi(\underline{r})} \right)^2 d\underline{r} \quad [9]$$

To solve [8] we need an expression for $\frac{\delta \Delta G_F}{\delta \phi(\underline{r})}$

From [2]:

$$\frac{\delta \Delta G_F}{\delta \phi(\underline{r})} = \frac{\partial g}{\partial \phi} - \epsilon^2 \nabla^2 \phi \qquad [10]$$

Substituting [10] into [8]:

$$\frac{\partial \phi(\underline{r})}{\partial t} = -M_\phi \left[\frac{\partial g}{\partial \phi} - \epsilon^2 \nabla^2 \phi \right] \quad [11]$$

Two components, one phase

We consider two components which can mix or seperate but which exist in a single phase

- We characterise the system by the conc. of one component at each position:
- $c(\underline{r})$ of component a in a small volume centred on point $\underline{r}$ is:

$$c(\underline{r}) = \frac{n_a(\underline{r})}{n_a(\underline{r}) + n_b(\underline{r})} \quad [12]$$

n_a => no. density of formula units of a in the vol

$0 < c < 1$ where $c = 0$ is pure b
$c = 1$ is pure a

If the total number of sites at which a and b can sit is N and the volume of the system is V then we have: $\frac{N}{V} = n_a(\underline{r}) + n_b(\underline{r})$

number density of available sites independent of position & distribution of components

Since the total number of particles N_a is conserved we have: $\int n_a(\underline{r}) d\underline{r} = N_a \quad [13]$
Substituting [12] into [13] then:

$$N_a = \frac{N}{V} \int c(\underline{r}) d\underline{r} \quad [14]$$

Defining avg. conc. by $\bar{c} = N_A / N$ then:

$$\bar{c} = \frac{1}{V} \int c(\underline{r}) d\underline{r} \qquad [15]$$

Assuming we know the free energy of formation per unit vol. of the bulk phases for each conc. $g(c)$, we also incorporate the surface term:

$$\Delta G_F = \int \left[g(c(\underline{r})) + \tfrac{1}{2}\epsilon^2 |\nabla c(\underline{r})|^2 \right] d\underline{r} \quad [15.1] \qquad // \text{ a functional of conc.}$$

Recalling the governing equation: $\frac{d\Delta G_F}{dt} \leq 0$ we get $$\frac{d\Delta G_F[c]}{dt} = \int \frac{\delta \Delta G_F}{\delta c(\underline{r})} \frac{\partial c(\underline{r})}{\partial t} d\underline{r} \quad [16]$$

$\bar{c}$ is a const, c is a conserved quantity & so we turn to the continuity equation

Numerical Solution

Based off CH-muSE

Stable, semi implicit method

Taking the Fourier transform of both sides of the equation : $\frac{\partial \tilde{c}(g,t)}{\partial t} = -g^2 \tilde{h}(g,t) - g^4 \tilde{c}(g,t)$

// $\tilde{h}(g,t) = \int h(x,t) e^{-igx} dx = \int c(1-c)(1-2c) e^{-igx} dx$

We make a finite difference approximation for the time derivative & exploit the implicit method for $\tilde{c}$ not $\tilde{h}$.

We obtain :

$$\frac{\tilde{c}(g, t+\Delta t) - \tilde{c}(g,t)}{\Delta t} \approx -g^2 \tilde{h}(g,t) - g^4 \tilde{c}(g, t+\Delta t)$$

Rearranged : $$\tilde{c}(g, t+\Delta t) \approx \frac{\tilde{c}(g,t) - g^2 \tilde{h}(g,t) \Delta t}{1 + g^4 \Delta t}$$