

Computational modelling of Multiphase flow

i) Models without explicit interface tracking

Mass conservation
Momentum balance
Energy conservation } industry (Bin lecture)

→ Particle simulations (one way coupling / two way coupling)

ii) Interface tracking / capturing methods

"Laplace" formalism

- Front Tracking method
- Boundary Integral / element method (Tak)

nodal points / markers track the interface evolution → boundary conditions

Volume of fluid } concentration based

- Level Set } ⇒ $\phi(x,t)$ is advected and represents the phases + interface

Gibbs / van der Waals formalism

- Lattice Boltzmann
- Phase Field (Exc. 3)

thermodynamic description of the system and phases

Pros	Cons
<ul style="list-style-type: none"> • Accurate calculation of surface tension • Compact mathematical description 	<ul style="list-style-type: none"> • Cannot handle topological change i.e. coalescence. • Challenging wetting boundary conditions - Harkens • Not intrinsically mass conserving (CVOF) • Challenging wetting bc's. • Rules for interface "reconstruction".
<ul style="list-style-type: none"> • High-density / viscosity contrasts • Accurate surface tension 	<ul style="list-style-type: none"> • computationally challenging to solve • Diffuse interface "smearing" of properties
<ul style="list-style-type: none"> • Compact mathematical description • Well defined wetting boundary conditions 	

Thermodynamic description of multiphase model

Start with a description of the systems free energy, monoatomic - binary phases

Thermodynamic quantities ; T - temperature, ρ - density, P - pressure
 e - internal energy,

Helmholz free energy density per volume (no interface)

$$f(\rho, T) = k_B T \frac{\rho}{m_p} \left[\ln \left(\frac{\frac{\rho}{m_p} T^{3/2}}{1 - b \frac{\rho}{m_p}} \right) - 1 \right] - a \left(\frac{\rho}{m_p} \right)^2$$

$\Delta = U - TS$
 Thermodynamic
 H : potential
 $V(\rho, T) = \text{const} (T = \text{const})$
 Gibbs:
 $\text{const.}(\rho, T)$
 $G(\rho, T) = U + PV - TS = H - TS$

k_B = Boltzmann const
 m_p = particle mass
 a, b - fluid specific constants

From the free energy we derive the van der Waals equation of state:

$$P(\rho, T) = \rho \frac{\partial f(\rho, T)}{\partial \rho} - f(\rho, T) = \frac{k_B T \frac{\rho}{m_p}}{1 - b \frac{\rho}{m_p}} - a \left(\frac{\rho}{m_p} \right)^2$$

Internal energy:

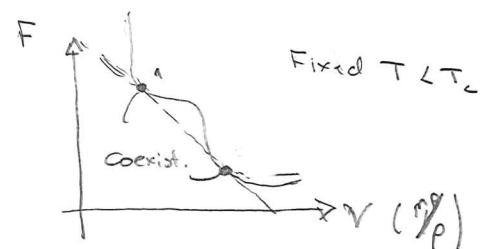
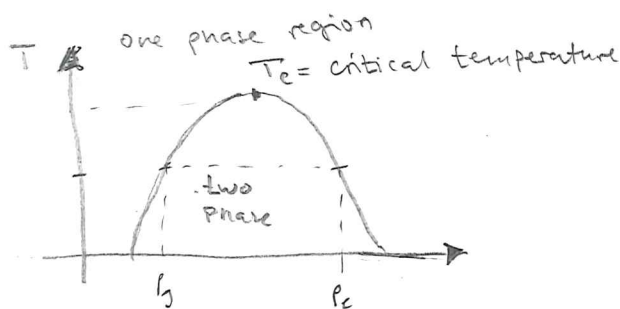
$$e(\rho, T) = f(\rho, T) - T \frac{\partial f(\rho, T)}{\partial T} = \frac{3k_B}{2m} T \rho - \frac{a}{m^2} \rho^2$$

Including an interface (van der Waals, Cahn-Hilliard ++, Ginzburg-Landau ++)

Total free energy:

$$F = \int_V \left(f(\rho, T) + \frac{\kappa}{2} |\nabla \rho|^2 \right) dV \rightarrow \text{minimize for } T = \text{const.}, \text{ for } \rho, \nabla \rho$$

\rightarrow Euler Lagrange equation, phase coexistence diagram.



• characteristic interface width arise from "first" principle description at thermodynamics and coexistence curve \rightarrow not fitting parameter \rightarrow nano-scale

How arrive at the free-energy description?

Approach by Cahn-Hilliard (1958), assume free energy density (f) to be a continuous function, $f(c, \nabla c, \nabla^2 c, \dots)$

Taylor expansion about f_0 ;

$$f(c, \nabla c, \nabla^2 c, \dots) = f_0(c) + \sum_i L_i \left(\frac{\partial c}{\partial x_i} \right) + \sum_{ij} K_{ij}^{(1)} \frac{\partial^2 c}{\partial x_i \partial x_j} + \frac{1}{2} \sum_{ij} K_{ij}^{(2)} \left[\frac{\partial c}{\partial x_i} \frac{\partial c}{\partial x_j} \right] + \dots$$

↑ polarization vector tensors

consider isotropic medium, symmetrically invariant $x_i \rightarrow -x_i$ (*)
 rotational symmetry (four fold axis) $x_i \rightarrow x_j$ (**)

(*) ^ (**) $\rightarrow L_i = 0$

$K_{ij}^{(1)} = K_{ij}^{(2)} = 0 \quad i \neq j$

$i=j, \quad K_{11}^{(1)} = K_1 = \frac{\partial^2 f_0}{\partial (\nabla^2 c)}$

$K_{11}^{(2)} = K_2 = \frac{\partial^2 f_0}{(\partial^2 c)^2}$ coefficients

Total free energy ; $F = N_v \int \left[f_0(c) + K_1 \frac{\partial^2 c}{\partial x_i^2} + \frac{K_2}{2} \left(\frac{\partial c}{\partial x_i} \right)^2 \dots \right] dV$
 ↑
 Particles per volume

$$\int K_1 \frac{\partial^2 c}{\partial x_i^2} dV = \int \frac{\partial K_1}{\partial x_i} \frac{\partial c}{\partial x_i} dV - \int K_1 \frac{\partial c}{\partial x_i} n_i dA$$

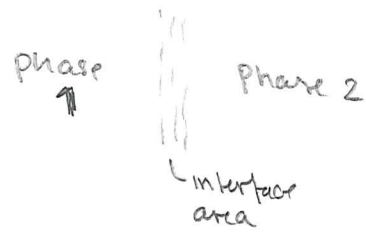
$= \int \frac{\partial K_1}{\partial c} \frac{\partial c}{\partial x_i} \frac{\partial c}{\partial x_i} dV$ assume no boundary term / flux in free energy.

$$= \int \frac{\partial K_1}{\partial c} \left(\frac{\partial c}{\partial x_i} \right)^2 dV$$

$$\rightarrow \frac{\partial K_1}{\partial c} + \frac{K_2}{2} = K/2$$

$$\Rightarrow F = N_v \int \left[f_0(c) + \frac{K}{2} \left(\frac{\partial c}{\partial x_i} \right)^2 \right] dV$$

Surface tension of a flat interface



$$F = A N_V \int_{-\infty}^{\infty} \left[f_0(c) + \frac{\kappa}{2} \left(\frac{\partial c}{\partial x} \right)^2 \right] dx$$

$$\gamma = N_V \int_{-\infty}^{\infty} \left[f_0(c) + \frac{\kappa}{2} \left(\frac{\partial c}{\partial x} \right)^2 \right] dx$$

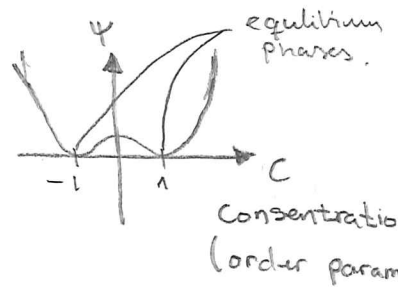
→ per definition difference per unit area of interface and which it would have if continuous throughout

Interpretation of free energy model for isothermal phases

→ Phase field / Diffuse interface model.

Describe $N_V f_0(c) = \beta \Psi(c)$

Mexican hat, double-well potential



One choice for $\Psi(c) = \frac{1}{4} (c+1)^2 (c-1)^2$

Rename $N_V \kappa = \alpha$, $\Rightarrow F = \int (\alpha \Psi(c) + \frac{\beta}{2} |\nabla c|^2) dV$

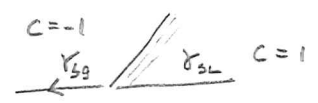
$$F = \int \left(\frac{\gamma}{\epsilon} \Psi(c) + \frac{\gamma \epsilon}{2} |\nabla c|^2 \right) dV$$

$F_{\Omega} = \text{bulk}$

$\Rightarrow c = []$
 $\alpha = \frac{N}{m^2}$
 $\beta = N m$
 γ / ϵ
 $\gamma \cdot \epsilon$
 Surface tension
 Caract length = interface width

What about energy of surface in contact with phase $c=1, c=-1$

$$F_{\Gamma} = \int (\gamma_{sg} + (\gamma_{sl} - \gamma_{sg}) g(c)) d\Gamma$$



$g(c=-1) = 0$
 $g(c=1) = 1$
 transition
 → find in homework

$$F = F_{\Omega} + F_{\Gamma}$$

$$\frac{\delta F}{\delta c} = \int \phi dV - \int \beta \epsilon \nabla c \cdot \underline{n} d\Gamma + \int (\gamma_{sl} - \gamma_{sg}) g'(c) d\Gamma$$

$\Rightarrow \epsilon \nabla c = \frac{\gamma_{sl} - \gamma_{sg}}{\gamma} \cos \theta_e$
 Boundary condition

$$= \underbrace{\int \frac{\gamma}{\epsilon} \Psi'(c) - \gamma \epsilon \nabla^2 c dV}_{\text{bulk}} - \underbrace{\int \beta \epsilon \nabla c \cdot \underline{n} d\Gamma + \int \gamma \cos \theta_e g'(c) d\Gamma}_{\text{boundary}}$$

Flux evolution, conservation of mass with variation δc

(4)

$$\frac{\delta c}{\delta t} = -\nabla \cdot \underline{j} \quad \rightarrow \underline{j} \text{ is a flux, } \underline{j} = -M \nabla \phi \quad \begin{array}{l} \nearrow \text{Chemical} \\ \text{Potential} \\ \uparrow \\ \text{"Mobility" / diffusivity} \end{array}$$

① $\frac{\partial c}{\partial t} + \underline{u} \cdot \nabla c = \nabla \cdot (M \nabla \phi)$ \rightarrow general conservation equation.

Must comply with the basic laws of thermodynamics
 • i.e. decrease of energy in time (increase of entropy.)

What is the sign of M for ∇ ? Assume $\underline{u} = 0$.

surface tension force (source term in Navier Stokes)

\rightarrow gradient of energy $\rightarrow \frac{\partial \gamma}{\partial x} = \frac{\partial \gamma}{\partial c} \frac{\partial c}{\partial x} = \phi \frac{\partial c}{\partial x} = \phi \nabla c \rightarrow$ couples to ①

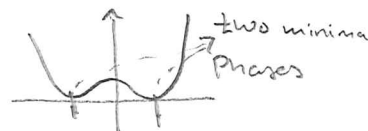
Phase separation of mixtures

Spontaneous phase separation of immiscible phases
 (spinodal decomposition) \rightarrow described by phase field.

Fastest growing mode? ($\underline{u} = 0$ + linear stability analysis.)

general form of $\psi_g = \frac{a}{2} c^2 + \frac{b}{4} c^4 + d$ $a < 0$

Use $c = c_0 + \xi e^{\beta t + i k x}$
 $\xi \ll c_0$



insert into CH eq. + linearize

$$\frac{\partial c}{\partial t} = M \nabla^2 \left(\frac{\delta \psi_g}{\delta c} - \gamma \nabla^2 c \right) = M \left(\nabla^2 \left[\frac{\delta}{\delta c} a \cdot c_0 \xi + \frac{\delta}{\delta c} b c_0^3 \xi \right] e^{\beta t + i k x} - \gamma \nabla^2 c \right)$$

$$\xi \beta e^{\beta t + i k x} = M e^{\beta t + i k x} \left[-\frac{k^2}{\epsilon} c_0 [a + 3b c_0] - \gamma \epsilon c_0 k^4 \right]$$

$$\beta = -M k^2 \gamma \epsilon \left[\frac{1}{\epsilon^2} [a + 3b c_0] + k^2 \right]$$

$a, b, c_0 < 0$

\rightarrow fastest growing mode $\frac{\partial \beta}{\partial k} = 0 \Rightarrow k = \left(-\frac{[a + 3b c_0]}{2 \epsilon^2} \right)^{1/2}$