Inclusive (almost!) application of numerical techniques in Materials Science

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Contents

Introduction

Topics to be covered

- Calculus of Variations: Minimize $\left[\int f(x, y, \frac{dy}{dx}, \cdots)dxdy\right] \implies \frac{d}{dx}\left(\frac{\partial f}{\partial y'}\right) - \frac{\partial U}{\partial y} = 0$

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- Finite Difference method (solving ODE's): $\frac{f_j^{n+1} - f_j^n}{k} = \frac{f_{j+1}^n - 2f_j^n + f_{j-1}^n}{h^2}$ (and BC)

A breif insight into Materials Science

- Materials, are **lazy** and have a general dislike towards **order**.
- The most stable form of a material is always that configuration which has the lowest **Gibbs Free Energy** (at a fixed temperature and pressure).

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- The most stable form of a material is always that configuration which has the lowest **Gibbs Free Energy** (at a fixed temperature and pressure).
- So in a nutshell, we try to ensure that the state of minimum G is the state we want and therefore control(engineer!) the constraints and parameters accordingly.

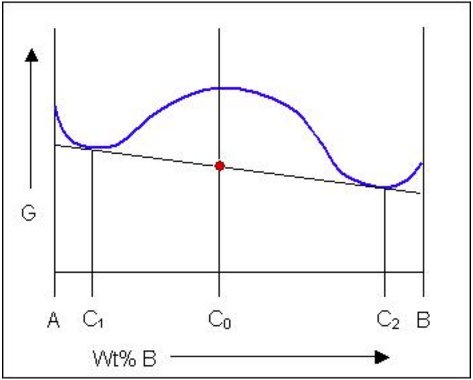

Figure: A typical free energy vs composition curve.

Problem Statement

Cahn-Hilliard Free energy functional

- The problem we are dealing with involves minimising a functional (which maps each composition to it's equivalent free energy $\rightarrow G(X_i)$. (the thermodynamics of the system)

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- We also want to follow the path of the composition change (locally) in the system as it slowly rearranges to the minimum energy configuration from the initial composition profile. (the kinetics of the system)

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Therefore the function to minimise is

$$F = \int \left[AX(1-X)(1-2X) + K\left(\frac{dX}{dx}\right)^2 - \underbrace{\alpha(X - X_o)}_{\text{const. total comp.}} \right] dx$$ [1]

Where A and K are material constants which uniquely identify a particular alloy system.

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Finding Material Constants

Schrödinger's equation(SE)

- In general, the first step to finding any material property is to solve the schrödinger's equation(SE) for the system. (which is an eigen value problem)

$$\underbrace{\left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]}_{\text{Hamiltonian}}\psi = E\psi \; ^{2} \qquad \text{compare to} \qquad Ax = \lambda x$$

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Density Functional Theory (For large practical systems)[3]

- Guess an initial ψ $\rightarrow$ construct the hamiltonian $\rightarrow$ minimise it using iterative algorithms such as **Gradient Search algorithm**
- Popular packages include VASP, Quantum Espresso...

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Rate equations

Fick's Law

The evolution equation is given by

$$\frac{\partial X}{\partial t} = M\nabla^2 \left(\frac{\partial F_{\text{min}}}{\partial x}\right) \text{ [4,5]}$$

M is also a material property (diffusivity)

[4] Annalen der Physik und Chemie von J. C. Pogendorff, 94, 59-86

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Some unavoidable gory math

- F_{min} at a given X, is given by the solution

$$\frac{\partial F_{\text{min}}}{\partial x} = \frac{df}{dX} - 2K\left(\frac{d^2X}{dx^2}\right)$$

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- Therefore the rate equation is given by

$$\frac{\partial X}{\partial t} = -M \left[\left(\frac{\partial^2 g}{\partial x^2} \right) - 2K \left(\frac{\partial^4 X}{\partial x^4} \right) \right] \text{ where } g = \frac{\partial f}{\partial X}$$

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Analysing the rate equation

$$\frac{\partial X}{\partial t} = -M\left[\left(\frac{\partial^2 g}{\partial x^2}\right) - 2K\left(\frac{\partial^4 X}{\partial x^4}\right)\right]$$

- 1 differential in time: $\left(\frac{\partial X}{\partial t}\right)$,
- 1 double differential in space: $\left(\frac{\partial^2 g}{\partial X^2}\right)$,
- 1 fourth order differential in space $\left(\frac{\partial^4 X}{\partial x^4}\right)$
- $g = \frac{\partial f}{\partial X}$ is a simple differential and can be evaluated analytically. At least in this problem.

Solving the equations

Dealing with space derivatives - Fourier Transforms

- We use the following trick:

$$\mathcal{F}\{f^n(x)\} = i^n k^n \mathcal{F}\{f(x)\}, \text{ where } k = \frac{2\pi x}{L} \text{is the reciprocal space vector [6]}$$

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- Therefore we all our variables to fourier space, the rate equation in fourier space is given by:

$$\frac{\partial \tilde{X}}{\partial t} = -M(k^2\tilde{g} + 2Kk^4\tilde{X}), \text{ where } \tilde{V} \text{ refer to the variables in the fourier space}$$

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Dealing with time derivative - Finite difference Scheme

- The discreetized equations have the form

$$\frac{\tilde{X}(k, t + \delta t) - \tilde{X}(k, t)}{\delta t} = -M[k^2\tilde{g}(k, t) + 2Kk^4\tilde{X}(k, t + \delta t)]$$

- In general for multiple components can be solved using any equation solving technique. NOTE. all variables in general are matrices and vectors

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Pseudo-Code

Input X, K, M, A
Choose $\Delta x, \Delta t$
Choose grid size n
Declare variables g
Set initial homogenous composition at each point
$\Delta k \longleftarrow {}^{2\pi n}/_{\Delta x}$
for index: 1 **to** timesteps **do**
    $g \leftarrow f(X)$
    $\tilde{g} \leftarrow \text{ForwardDFT}(g)$
    $\tilde{c} \longleftarrow \text{ForwardDFT}(c)$
    for i1: 1 **to** n **do**
        if i $< n$ **then**
            $k = i1\Delta k$
        else
            $k = (i1 - n)\Delta k$
        end if
    end for
    $\text{SolveEq}(k^2, k^4, g, X, \Delta t)$
    $g \leftarrow \text{BackwardDFT}(\tilde{g})$
    $X \leftarrow \text{BackwardDFT}(\tilde{X})$
end for