Diffuse Interface Models

M. Ceriotti - MSE304

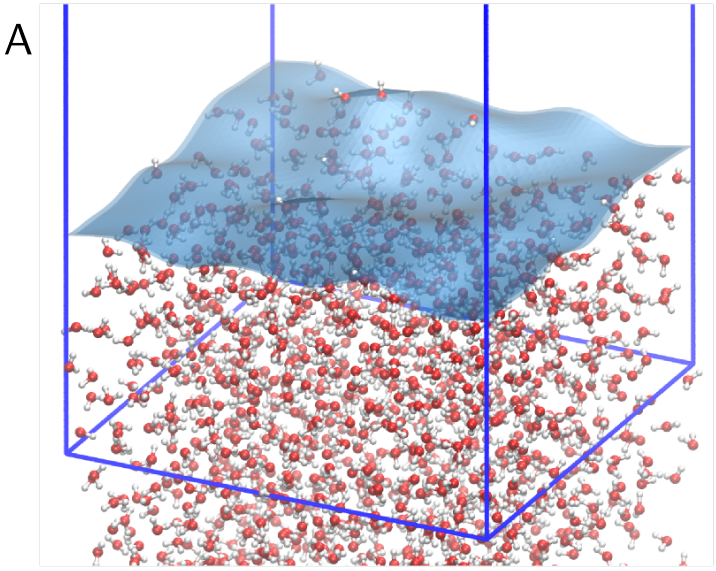
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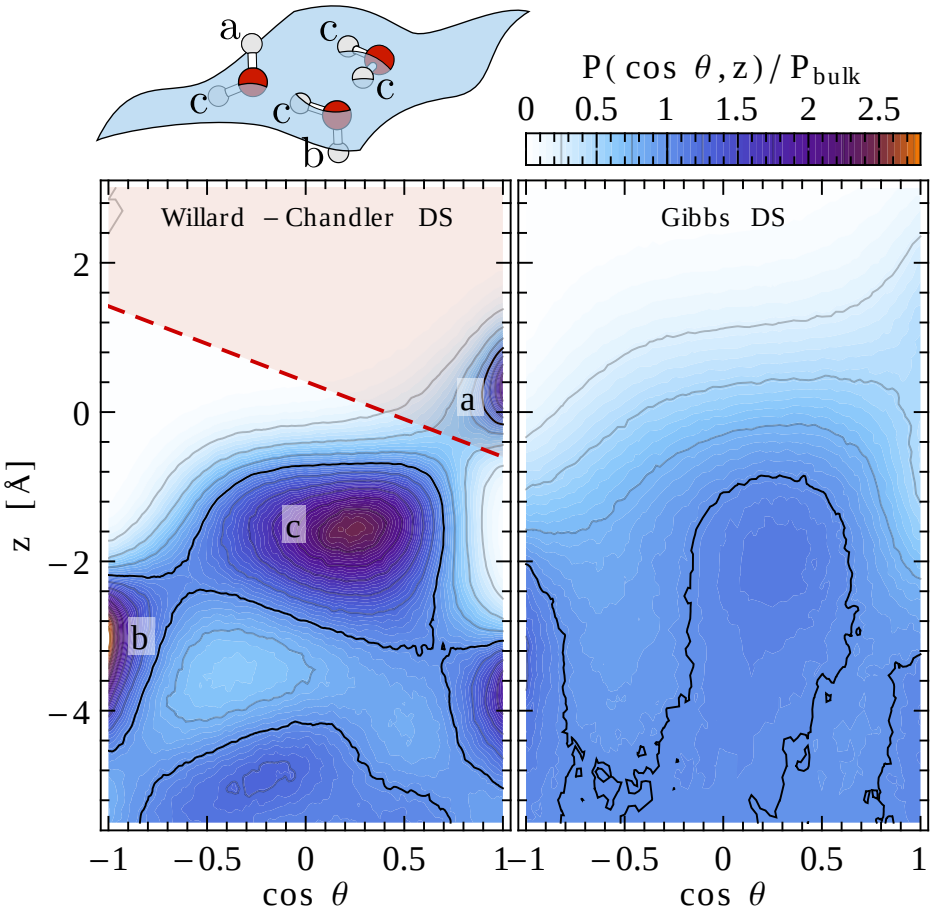
Outline

- Surface of liquids
- The Gibbs isotherm
- A reminder on regular solutions
- Cahn-Hillard model of phase segregation
- Diffusion and the dynamical behavior of the Cahn-Hillard model

Surface of Liquids

- How does a liquid surface look like at the atomic scale?

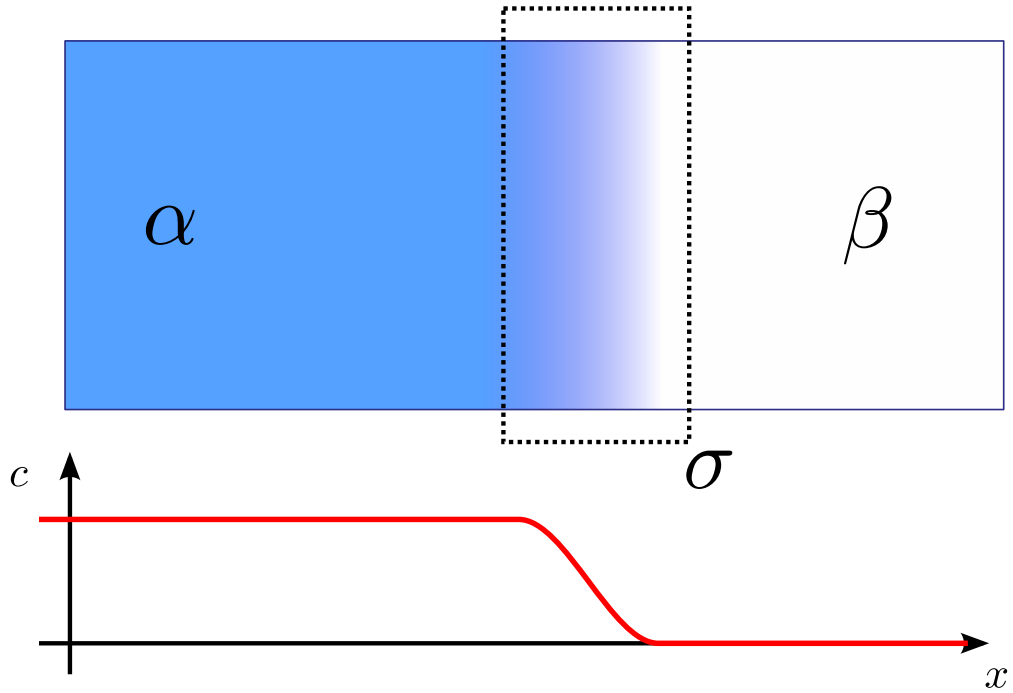




Gibbs Dividing Surface

- One can see the surface as a smooth transition between two bulk phases α and β
  - It is arbitrary to define a surface volume.
  - We can as well just assume $V^\alpha + V^\beta = V$, and introduce a surface excess $N^\sigma = \Gamma A$, which is still arbitrary
  - *Define* σ as the surface corresponding to $\Gamma = 0$

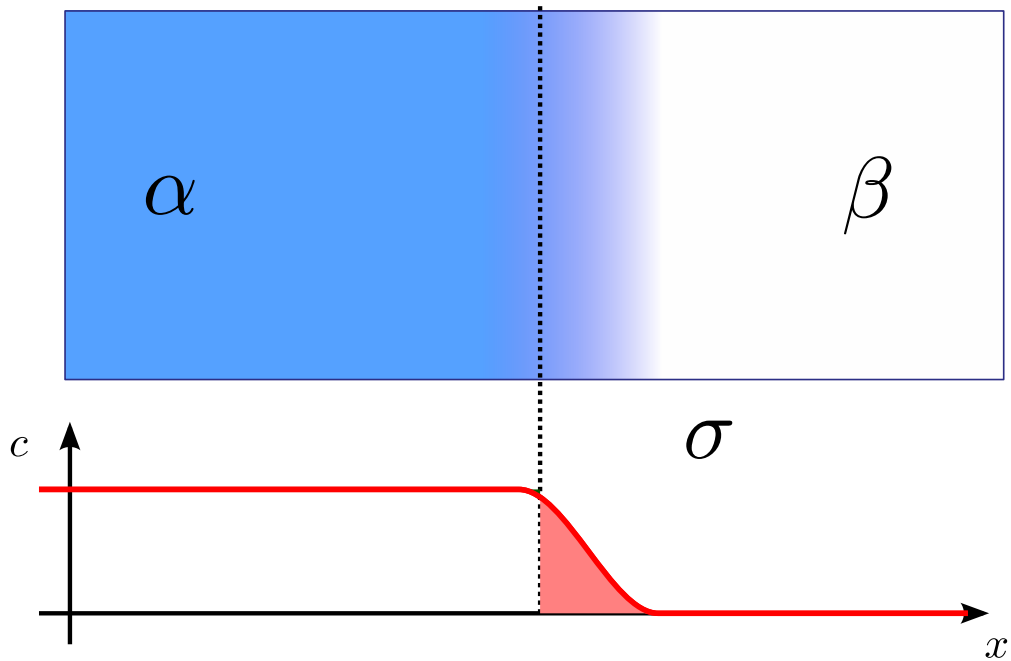
$$N = c^\alpha V^\alpha + c^\beta V^\beta + V^\sigma \langle c \rangle_\sigma$$



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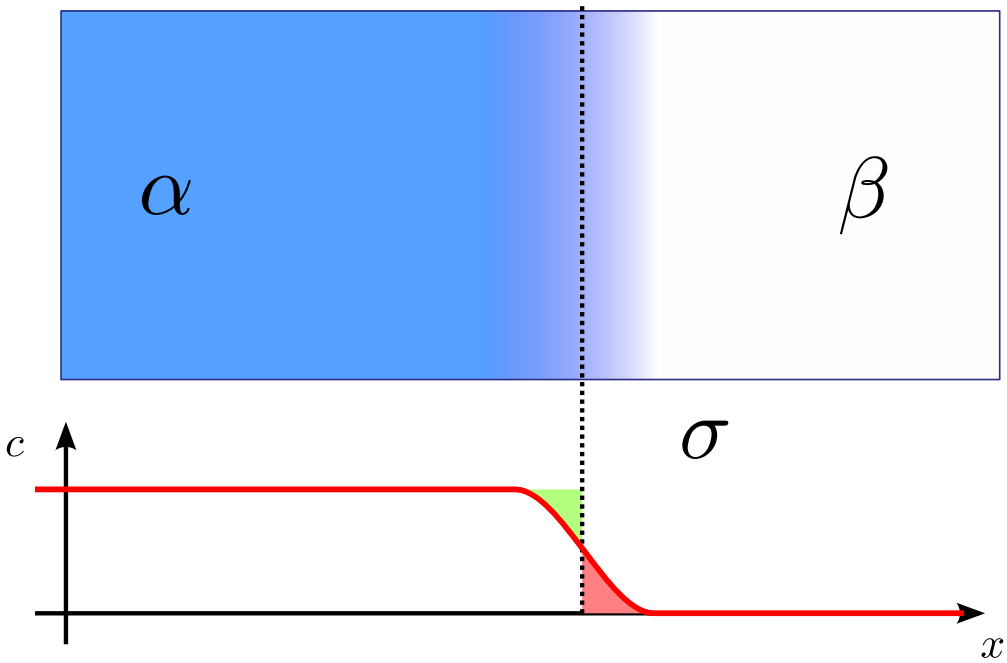
$$N^\sigma = V^\sigma \langle c \rangle_\sigma = \Gamma A = N - c^\alpha V^\alpha - c^\beta V^\beta$$



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$$N = c^\alpha \left(V - V^\beta\right) + c^\beta V^\beta$$



Multi-component Systems

- Consider multiple substances, each with a total number of molecules N_i. The surface excess of each component has still an arbitrary dependence on V^β

$$A\Gamma_i = N_i - c_i^\alpha V^\alpha - c_i^\beta V^\beta = N_i - c_i^\alpha V + \left(c_i^\alpha - c_i^\beta\right) V^\beta$$

- How can we define a quantity that does not depend on the choice of dividing surface? **Relative excess**

$$A\Gamma_i^{(1)} = A\Gamma_i - A\Gamma_1 \frac{c_i^\alpha - c_i^\beta}{c_1^\alpha - c_1^\beta} = N_i - c_i^\alpha V - (N_1 - c_1^\alpha V) \frac{c_i^\alpha - c_i^\beta}{c_1^\alpha - c_1^\beta}$$

- $\Gamma_i^{(1)}$ is the surface excess corresponding to the dividing surface that sets $\Gamma_1 = 0$

Gibbs Adsorption Isotherm

- The differential form for the surface internal energy can be written as

$$\mathrm{d}U^{\sigma} = \sum_i \mu_i \mathrm{d}N_i^{\sigma} + T\mathrm{d}S^{\sigma} + \gamma \mathrm{d}A$$

  - These are all extensive variables, so one can integrate to a finite system size to obtain

$$U^{\sigma} = \sum_i \mu_i^{\sigma} N_i^{\sigma} + \gamma A + TS$$

- Comparison with the total differential form reads at constant T

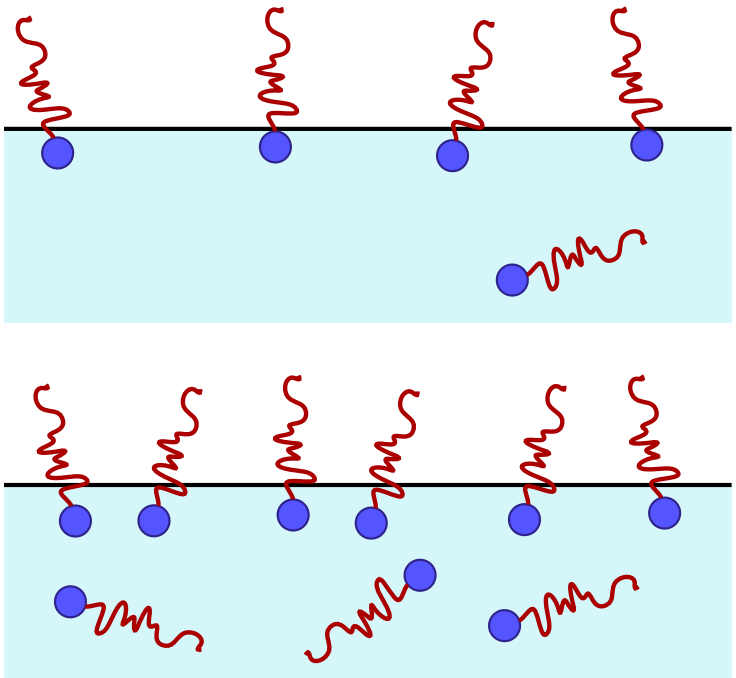
$$\boxed{\mathrm{d}\gamma = -\sum_i \Gamma_i \mathrm{d}\mu_i = -\sum_i \Gamma_i RT \frac{\mathrm{d}c_i}{c_i}}$$ Gibbs's Adsorption Isotherm

Implications of the Gibbs Isotherm

- Adding substances with a surface affinity ($\Gamma > 0$) *decreases* the surface tension of a liquid.

$$\mathrm{d}\gamma = -RT\frac{\Gamma}{c}\mathrm{d}c$$

- This is because to increase the surface one has to sequester more molecules from the bulk, which is made easier by increasing the bulk concentration



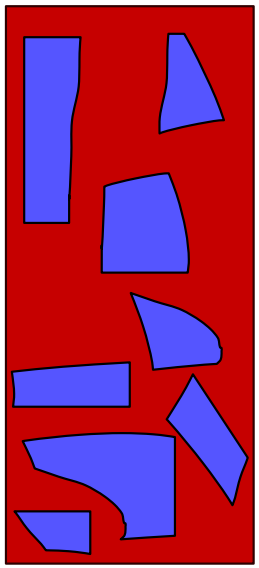
$$\Gamma > 0 \Rightarrow \frac{\partial \gamma}{\partial c} < 0$$

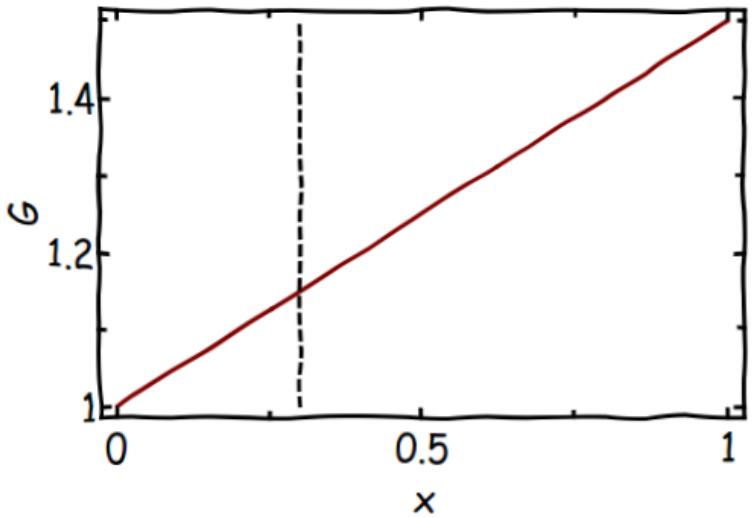
Regular Solution Model - A Reminder

- Take x_A moles of compound A, and $x_B = 1 - x_A$ moles of compound B, and **physically** mix them
- Assume only the entropy of solution matters (**ideal solution**)

$$\mu_{A,B} = \mu^{\ominus}_{A,B} + RT \ln x_{A,B}$$

- Add an enthalpy of mixing term $\Omega x_A x_B$ (**regular solution**)





$$\mu^{\ominus}_{A} = 1 \qquad \mu^{\ominus}_{B} = 1.5$$

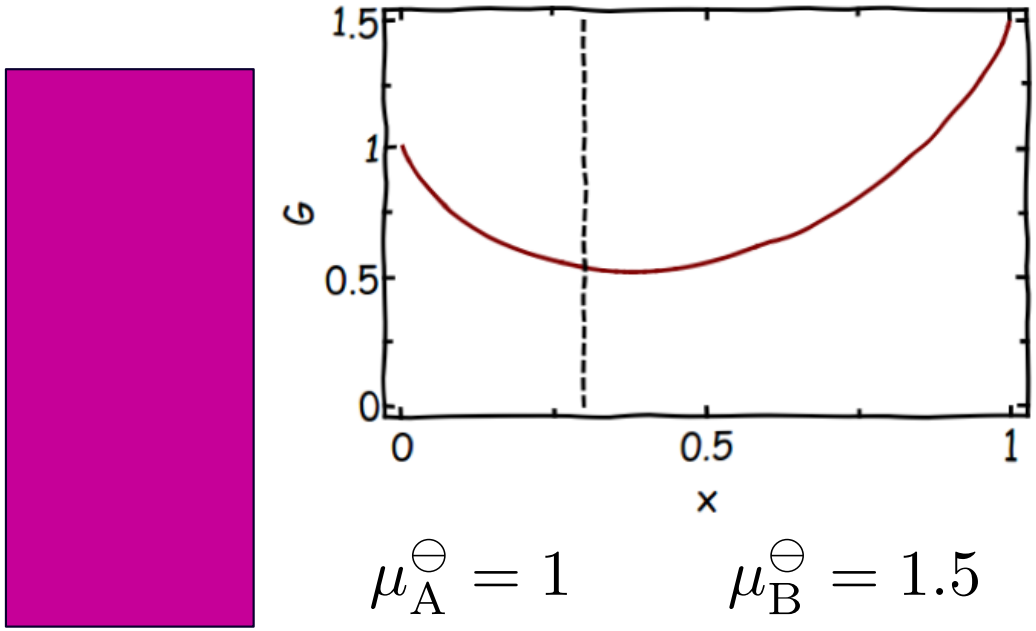
$$G = x_A \mu^{\ominus}_{A} + (1 - x_A)\, \mu^{\ominus}_{B}$$

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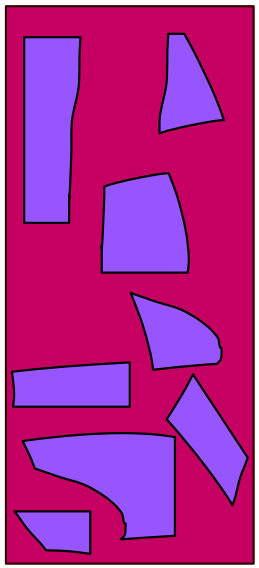
$$G = x_A \left(\mu^{\ominus}_{A} + RT \ln x_A\right) + (1 - x_A) \left(\mu^{\ominus}_{B} + RT \ln (1 - x_A)\right)$$

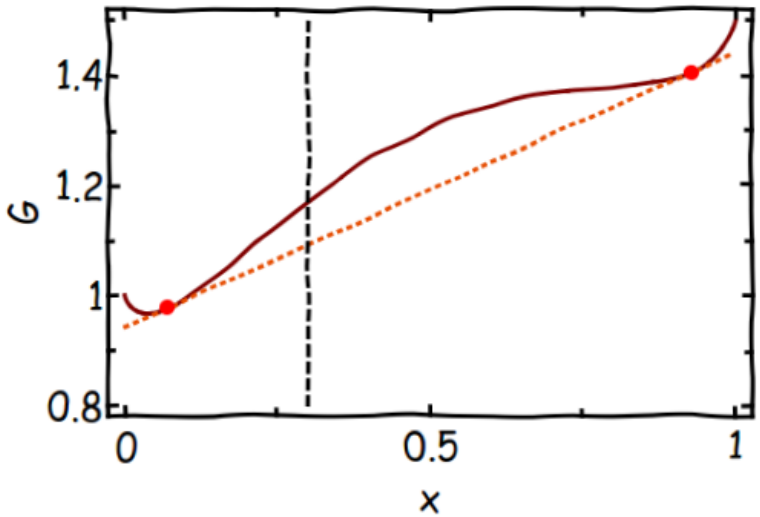
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- Add an enthalpy of mixing term $\Omega x_A x_B$ (**regular solution**)





$$\mu^{\ominus}_{A} = 1 \qquad \mu^{\ominus}_{B} = 1.5$$
$$RT = 1 \qquad \Omega = 2.5$$

$$G = x_A \left(\mu^{\ominus}_{A} + RT \ln x_A\right) + (1 - x_A)\left(\mu^{\ominus}_{B} + RT \ln (1 - x_A)\right) + \Omega x_A (1 - x_A)$$

A Thermodynamic Model of Interfaces

- We define a *local* molar free energy g, that depends on the local concentration, its gradient,etc. Then one can expand it in a Taylor series. . . and consider the symmetries that would arise in an isotropic system

$$G = \rho \int_V g\left(c, \nabla c, \nabla^2 c, \ldots\right) \mathrm{d}V$$

$$g_0\left(c\right) + \frac{\partial g}{\partial \nabla_i c}\nabla_i c + \frac{\partial g}{\partial \nabla^2 c}\nabla^2 c + \frac{1}{2}\nabla_i c \frac{\partial^2 g}{\partial \nabla_i c \partial \nabla_j c}\nabla_j c + \ldots$$

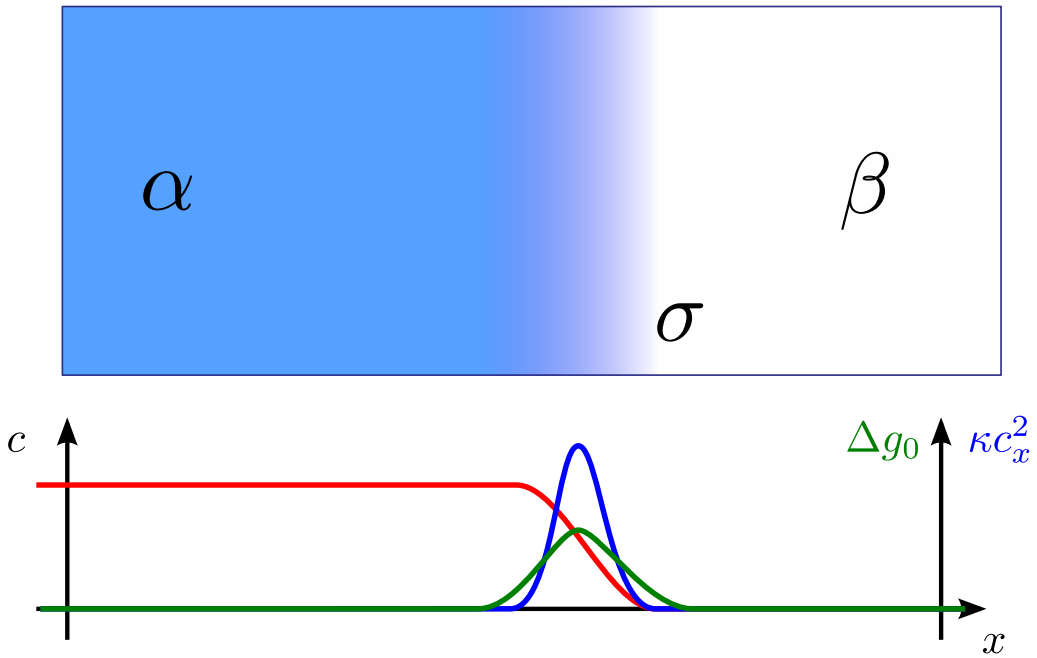
$$\boxed{G = \rho \int_V g_0\left(c\right) + \kappa \left|\nabla c\right|^2 \mathrm{d}V}$$ Cahn-Hilliard Equation

$$\kappa = \left.\frac{\partial^2 g}{\partial \left|\nabla c\right|^2}\right|_0 - \left.\frac{\partial^2 g}{\partial c \partial \nabla^2 c}\right|_0$$

Excess Free Energy of an Interface

- Now consider a 1D interface between two phases α and β. If the system was homogeneous the free energy would be

$$G_0 = \int_V c(x)\,\mu_A + (1 - c(x))\,\mu_B dx$$

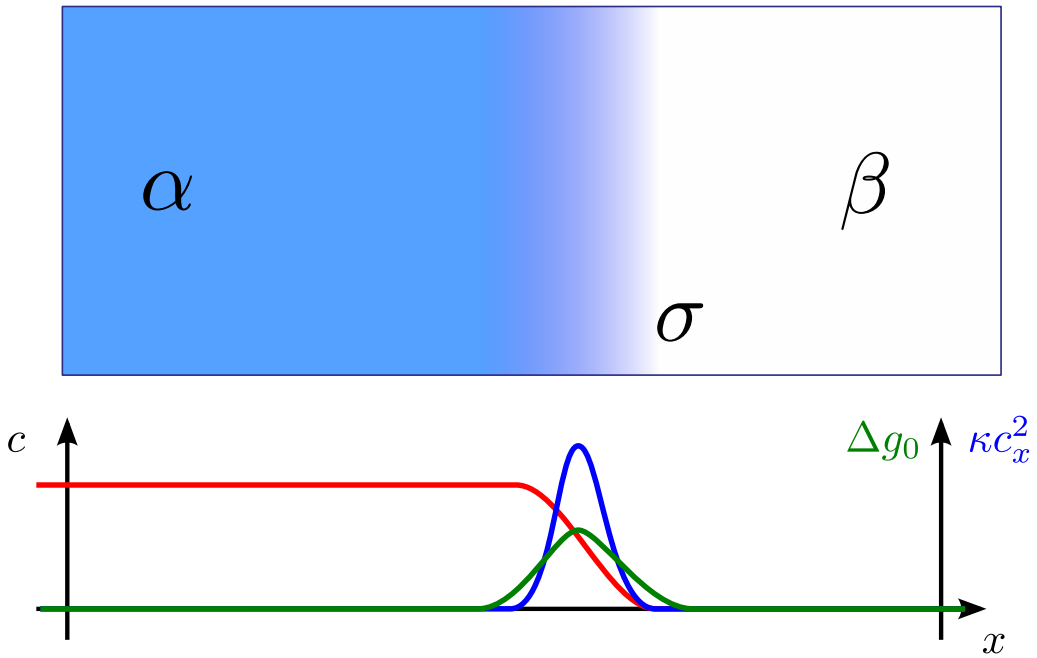


Excess Free Energy of an Interface

- We can define an excess free energy associated with the interface

$$\Delta G = \rho \int \Delta g_0 (c) + \kappa |c'|^2 \, \mathrm{d}x, \qquad \Delta g_0 = g_0 (c) - c\mu_A - (1 - c)\, \mu_B$$

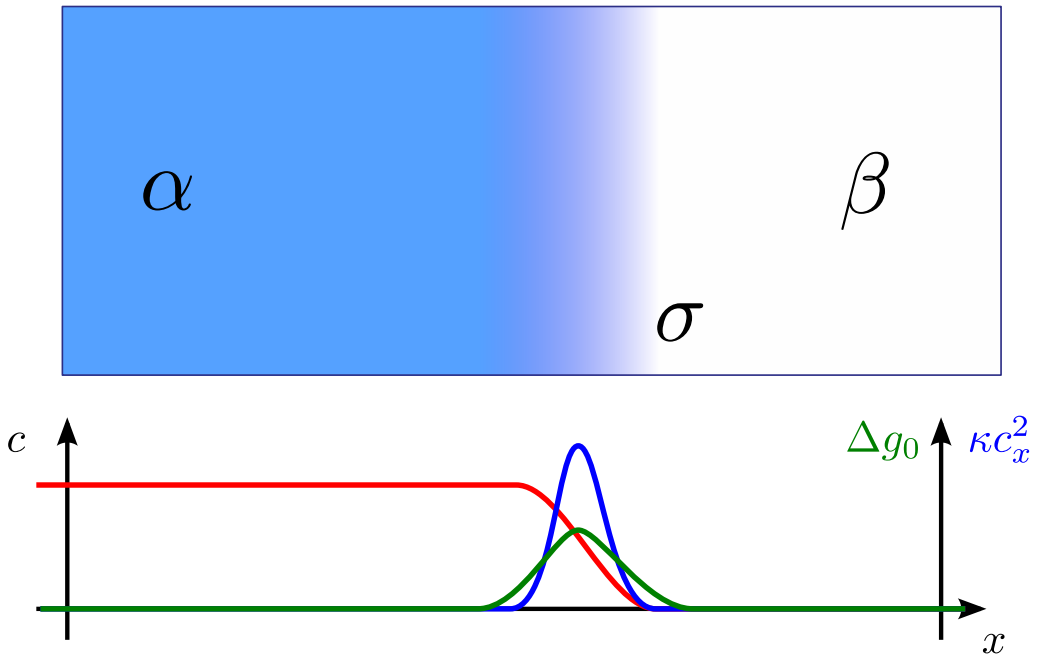
- A more diffuse interface (small $|c'|$) reduces the free energy, but has a larger region with non-equilibrium concentrations.



Excess Free Energy of an Interface

- One can obtain the equilibrium interface shape by *calculus of variations*:

$$\frac{\delta \Delta G}{\delta c} = 0 \rightarrow K = \Delta g_0(c) + \kappa c'^2 - c'(2\kappa c') \rightarrow \Delta g_0(c) - K = \kappa c'^2$$

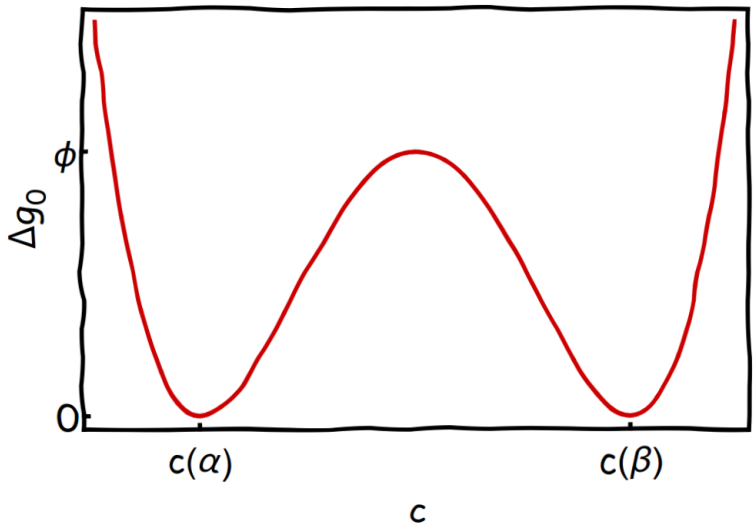


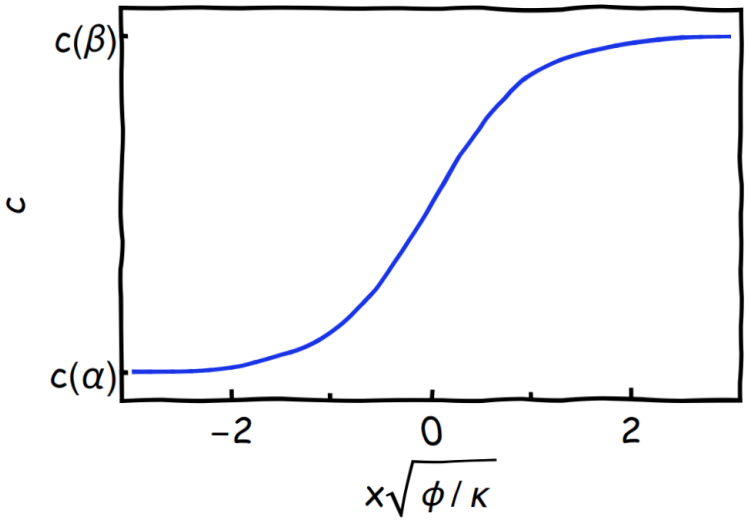
A Simplified Solution for the Interface

- Let's try a simple model for the excess free energy, $\Delta g_0(c) = \phi\left(c^2-1\right)^2$

$$\kappa c_x^2 = \phi\left(c^2-1\right)^2 \rightarrow \sqrt{\frac{\kappa}{\phi}}\frac{\partial c}{\partial x} = \pm\left(c^2-1\right) \rightarrow c(x) = \pm\tanh x\sqrt{\frac{\phi}{\kappa}}$$

- One can also evaluate the free energy associated with the interface
  - With this simplified model, $\Delta G = \frac{\rho}{6}\left(c(\beta)-c(\alpha)\right)^3\sqrt{\phi\kappa}$





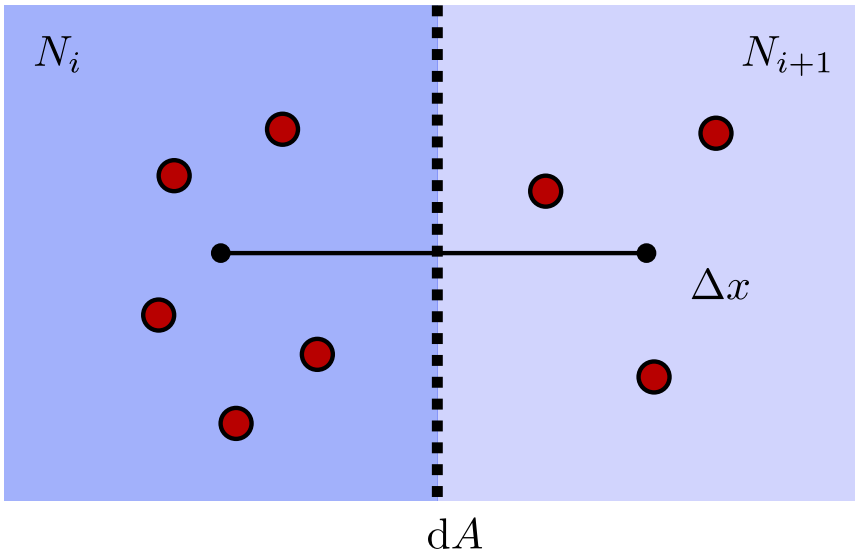
$$\Delta G = 2\rho\int \Delta g_0(c)\,dx = 2\rho\kappa\int \frac{\partial c}{\partial x}\frac{\partial c}{\partial x}dx = 2\rho\sqrt{\kappa}\int_{c(\alpha)}^{c(\beta)}\sqrt{\Delta g_0(c)}dc$$

Fick's Law - A Reminder

- Discretized flux across the interface is proportional to the number of particles in each volume
- Can be generalized to many dimensions and a non-ideal solutions
- Continuity equation imposes balance between concentration and flux

$$j\mathrm{d}A = \frac{k}{2}\left[N_i - N_{i+1}\right] = \frac{k}{2}\mathrm{d}A\Delta x\left[c\left(-\Delta x/2\right) - c\left(\Delta x/2\right)\right]$$

$$\boxed{\mathbf{j} = -D\nabla\mu} \qquad 1^{st}\text{Fick's law}$$



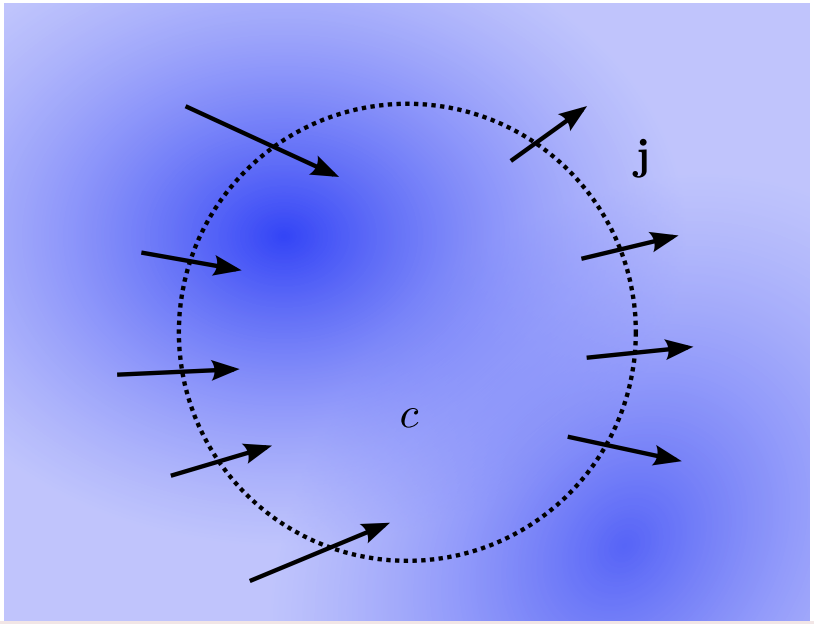
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$$\frac{\partial}{\partial t}\int_V c\,\mathrm{d}V = -\int_{\delta V}\mathbf{j}\cdot\hat{\mathbf{n}}\,\mathrm{d}A = -\int_V \nabla\cdot\mathbf{j}\,\mathrm{d}V$$

$$\boxed{\frac{\partial c}{\partial t} = -\nabla\cdot\mathbf{j} = D\nabla^2\mu}$$

2^{nd} Fick's law



Dynamics of the C-H Model

- Get the chemical potential as a functional derivative of the free energy of the Cahn-Hilliard model

$$\frac{\partial c}{\partial t} = D\nabla^2\mu = D\nabla^2\left[\frac{\partial \Delta g_0}{\partial c} - 2\kappa\nabla^2 c\right]$$

- Dynamical C-H equation is a model of *spinodal decomposition*

